


|   |        |
|---|--------|
| DELHI COLLEGE OF ENGINEERING  |        |
|  |        |
| LIBRARY   |        |
| Kashmiri Gate, Delhi-110006   |        |
| Accession No.   | 160710 |
| Class No.   | 691.5  |
| Book No.  | 701    |

**Borrower is requested  
to check the book and  
get the signatures on the  
torned pages, if any.**

# **DELHI COLLEGE OF ENGINEERING**

**Kashmiri Gate, Delhi-110006**

## **L I B R A R Y**

### **DATE DUE**

For each day's delay after the due date a fine of  
**10 Paise** per Vol. shall be charged for the first week, and  
**50 Paise** per Vol. per day for subsequent days.

---

| Borrower's<br>No. | Date Due. | Borrower's<br>No. | Date Due |
|-------------------|-----------|-------------------|----------|
|-------------------|-----------|-------------------|----------|





McGRAW-HILL PUBLICATIONS IN AERONAUTICAL SCIENCE

JEROME C. HUNSAKER, *Consulting Editor*

EXPLOSION AND  
COMBUSTION PROCESSES  
IN GASES

*The quality of the materials used in  
the manufacture of this book is gov-  
erned by continued postwar shortages.*

McGRAW-HILL PUBLICATIONS  
IN AERONAUTICAL SCIENCE  
*Jerome C. Hunsaker, Consulting Editor*

*Jost-Croft*  
EXPLOSION AND COMBUSTION  
PROCESSES IN GASES

*Von Mises*  
THEORY OF FLIGHT

# EXPLOSION AND COMBUSTION PROCESSES IN GASES

BY WILHELM JOST, DR. NAT. SC.

PROFESSOR AT THE PHYSICAL CHEMISTRY INSTITUTE  
UNIVERSITY OF LEIPZIG

PUBLISHED AND DISTRIBUTED IN THE PUBLIC INTEREST  
BY AUTHORITY OF THE ALIEN PROPERTY CUSTODIAN UNDER  
LICENSE NUMBER A-953

TRANSLATED BY HUBER O. CROFT

HEAD OF THE DEPARTMENT OF MECHANICAL ENGINEERING  
THE STATE UNIVERSITY OF IOWA

IOWA CITY

FIRST EDITION  
SECOND IMPRESSION

---

McGRAW-HILL BOOK COMPANY, INC.

NEW YORK AND LONDON

1946

EXPLOSION AND COMBUSTION PROCESSES IN GASES

*All rights, especially that of translation into foreign languages, reserved.  
Copyright vested in the Alien Property Custodian, 1943, pursuant to law.*

COPYRIGHT, 1946, BY THE  
MCGRAW-HILL BOOK COMPANY, INC.

PRINTED IN THE UNITED STATES OF AMERICA

*All rights reserved. This book, or  
parts thereof, may not be reproduced  
in any form without permission of  
the publishers.*

THE MAPLE PRESS COMPANY, YORK, PA.

## PREFACE

The purpose of the present volume at the time it was planned was to present the experimental and theoretical facts underlying explosion and combustion processes in gases so thoroughly that the book would not only serve as an introduction to the field but also be of practical use to anyone working in similar branches of research.

When the work was begun, the excellent monograph by Lindner (1931) was the only one available in German. It dealt with the same subject but was intended to give only a brief survey. There are, of course, the English books by Bone, but they are obsolete, even though still of value for orienting the reader in older works on the subject, especially those in English. When the manuscript was almost finished, an English monograph by Lewis and von Elbe appeared, as well as a series of articles on combustion in the fourth volume of the handbook "The Science of Petroleum." The appearance of this monograph in no way makes the present volume superfluous, since, in addition to the fact that no German work exists on this subject, the author believes his book justified by the nature of its aim. He wishes to acknowledge that he has found these discussions very stimulating. Subjects treated exhaustively by Lewis and von Elbe that are of limited interest here have been purposely abridged in the present work.

In general, an effort has been made not only to give the theoretical basis but also to describe the experiments in such detail as to enable the reader to draw his own conclusions independent of the special theories of the author. The result has been that a sharp, systematic division was possible only in those chapters treating relatively well defined fields of research. In other fields—for instance, coal combustion—a somewhat roundabout manner of presentation was adopted so that the experiments of the various authors could be treated individually and theoretical considerations would not cause certain data to be stressed at the expense of others.

In this field of research, it happens again and again that data can be found in the literature that seem simultaneously to prove or to disprove theories that have been advanced. For this reason, although absolute completeness in the material to be presented was out of the question, completeness in the description of data differing qualitatively was striven for whenever possible. Because of the many factors that come into consideration in combustion reactions, the data of various authors may

appear to be mutually exclusive, a fact that does not imply, however, that any set of data is on that account unreliable. In attempting to incorporate data into a fixed theoretical system, there is always the danger of slighting important experiments.

To aim at completeness in the pertinent literature would have expanded this volume unduly. The author therefore contented himself with drawing only upon the more recent works with any degree of completeness. Older works not treated here may be found in the survey of the field given at the conclusion of this work.

Even though an attempt was made to present the facts as objectively, as possible, the author is not unmindful of the importance of theory for a mastery of the material presented here, as well as for any further development in this field of research. For that reason, theoretical considerations of the various processes have been given ample space. Moreover, these theories have not been presented without comment. On the contrary, the limits and weaknesses of present developments have been exposed, and suggestions have been made for further developments. Considering the extent of the material covered, the occasional omission of important references could not be avoided.

The field of combustion can be of equal interest to the engineer, the chemist, the physicist, and the physical chemist. For this reason, only the amount of knowledge shared by these various readers has been taken for granted in important passages of this book. Thus, for example, various elementary statements have been added to the fundamentals on reaction kinetics. Naturally, therefore, some portions will seem trivial to some and difficult to others. The aim was to fix upon a manner of presentation that would make the book comprehensible without the aid of other volumes, some of which are not easily accessible. In addition, of course, it was intended to furnish as much information as possible.

It is not assumed that the reader will read the entire book or even individual chapters consecutively, but rather that substantial portions dealing with specific theories or experimental detail (partly indicated by small print) will be skipped at a first reading and that the contents of other chapters will be referred to only insofar as they may be of aid in clarifying some point. Numerous references within the text as well as the additional references at the end of the book, which have been made as complete as possible, should be of aid in orienting the reader.

The succession of the individual chapters was determined, among other things, by the fact that all matters demanding a more detailed treatment of reaction kinetics were relegated to the second half of the book, since this field of research is probably least familiar to most readers.

All basically different processes (like coal-dust combustion, for example) and the chemical aspects of these phenomena had to be omitted.

For orientation in these fields, the references at the end of the book may be of value.

During the writing of this book, the author received suggestions and criticisms from many friends and colleagues. The supplementary material for the first chapter was prepared by Dr. L. v. Müffling. Dr. Rögner prepared the table of contents. Both gentlemen, as well as Dipl.-Eng. Teichmann helped read the proofs. To all of these the author is deeply grateful.

W. Jost.

LEIPZIG, GERMANY,  
*June, 1935.*





## TRANSLATOR'S PREFACE

The translation of this important work was undertaken by the publisher and the undersigned at the suggestion of Dr. W.F. Durand of the NACA and Dean E.A. Moreland of the NDRC because American engineers concerned with the development of the basic theories of combustion are naturally interested in some of the applications of physical chemistry to this problem as advocated by Dr. Jost.

The literal translation was prepared under the direction of Dr. F.L. Fehling of the University of Iowa department of German. Transformation to smooth English has occasionally been sacrificed where a literal translation expresses more faithfully the precise meaning intended by the author.

A brief table of conversion units for transformation from c.g.s. to f.p.s. units has been included (page xv) for those accustomed to the latter system of units.

Several obvious errors in the original work have been corrected, but no doubt others have escaped attention; and, of course, some new errors will be introduced by the very mechanics of the translation of a difficult scientific work. The publishers and the translator will consider it a favor if errors appearing in the published translation are called to their attention.

HUBER O. CROFT.

IOWA CITY, IOWA,  
*October, 1946.*



# CONTENTS

|   |     |
|---|-----|
| <i>Author's Preface</i> . . . . .   | v   |
| <i>Translator's Preface</i> . . . . .   | ix  |
| <i>Conversion Table for F.P.S. Units</i> . . . . .  | xv  |
| <i>Introduction</i> . . . . .   | 1   |
| CHAPTER I: INITIAL STAGES OF EXPLOSIONS (AUTO-IGNITION) AS A  |     |
| THERMAL PHENOMENON. . . . .   | 3   |
| 1. Preliminary Remarks . . . . .  | 3   |
| 2. Auto-ignition (Thermal Explosions). . . . .  | 4   |
| 3. Detailed Discussion of the Explosion Equations . . . . .   | 14  |
| 4. Examples of Thermal Explosions . . . . .   | 19  |
| 5. Ignition by Heated Surfaces. . . . .   | 21  |
| Supplement: Discussion of Experimental Data on Ignition Temperature<br>(by L. v. Müffling) . . . . .      | 32  |
| CHAPTER II: SPARK IGNITION I: THERMAL THEORY OF SPARK   |     |
| IGNITION . . . . .  | 47  |
| 1. Basic Facts and Statement of the Problem . . . . .   | 47  |
| 2. Expressions for a Simplified Quantitative Treatment . . . . .  | 49  |
| 3. Discussion of Experiments on Spark Ignition from the Standpoint of<br>the Theory of Heat . . . . .     | 56  |
| CHAPTER III: PROPAGATION OF EXPLOSIONS. . . . .   | 62  |
| 1. General Remarks . . . . .  | 62  |
| 2. Normal Velocity of Combustion . . . . .  | 65  |
| 3. Extended Theory of the Bunsen Flame . . . . .  | 74  |
| 4. Methodology for Determining Normal Combustion Velocity, Accord-<br>ing to Gouy and Michelson . . . . . | 84  |
| 5. Propagation of Combustion in Tubes . . . . .   | 91  |
| 6. Theory of Flame Propagation . . . . .  | 105 |
| 7. Reaction Velocity and Normal Velocity of Combustion . . . . .  | 120 |
| 8. Limits of Ignition . . . . .   | 124 |
| 9. Influence of Mixtures on Ignition Limits . . . . .   | 133 |
| CHAPTER IV: EXPLOSIONS IN CLOSED CHAMBERS. . . . .  | 136 |
| 1. Summary of Flame Propagation Phenomena in Closed Chambers. . .   | 136 |
| 2. Rate of Increase in Pressure and Flame Velocity. . . . .   | 144 |

|  |     |
|--|-----|
| 3. Theory of Pressure Increase and Temperature Gradient in Bomb Explosions, According to Mache . . . . . | 148 |
| 4. Specific Observations in Bomb Explosions . . . . .  | 156 |
| <b>CHAPTER V: DETONATION.</b> . . . .  | 160 |
| 1. Special Phenomena in Very Rapid Flames. Detonation . . . . .  | 160 |
| 2. Shock Wave and Detonation . . . . .   | 163 |
| 3. Experimental Determination of Detonation Velocities . . . . .   | 173 |
| 4. Detonation Limits . . . . .   | 181 |
| 5. Influence of External Factors on Induction and Propagation of Detonation . . . . .                    | 185 |
| 6. Detonation Pressures . . . . .  | 188 |
| 7. Influence of Additions on the Origin of Detonation. . . . .   | 190 |
| 8. Relation between Percussion Wave and Detonation: "Spin" of Detonations . . . . .                      | 192 |
| 9. Supplementary Material to the Theory of Detonation Processes. . . . .                                 | 201 |
| <b>CHAPTER VI: FLAMES OF GASES NOT PREMIXED</b> . . . . .  | 210 |
| <b>CHAPTER VII: FLAME TEMPERATURES. RADIATION INVESTIGATIONS ON FLAMES.</b> . . . .                      | 219 |
| 1. Measuring Flame Temperatures . . . . .  | 219 |
| 2. Calculating the Maximum Flame Temperatures . . . . .  | 224 |
| 3. Spectroscopic Analysis of Flames. . . . .   | 229 |
| 4. Thermal Radiation and Chemiluminescence . . . . .   | 235 |
| 5. Radiation and Temperature in the Engine . . . . .   | 239 |
| <b>CHAPTER VIII: KINETICS OF COMBUSTION AND EXPLOSION PROCESSES</b> 242                                  |     |
| 1. Fundamentals of Chemical Kinetics. . . . .  | 242 |
| 2. Kinetic Theory of Gases . . . . .   | 247 |
| 3. Chain Reactions Illustrated by the Example of the Reaction between Bromine and Hydrogen . . . . .     | 258 |
| 4. Reactions with Chain-branching . . . . .  | 264 |
| 5. The Time Element in the Development of a Chain Explosion. . . . .                                     | 280 |
| 6. Examples of Chain Explosions. . . . .   | 283 |
| <b>CHAPTER IX: COMBUSTION OF OXYGEN-HYDROGEN MIXTURES AND CARBON MONOXIDE.</b> . . . .                   | 292 |
| <b>A. Combustion of Oxygen-hydrogen Mixtures.</b> . . . .  | 292 |
| 1. The Lower Explosion Limit . . . . .   | 293 |
| 2. The Upper Explosion Limit . . . . .   | 299 |
| 3. Reaction outside the Explosion Limits. . . . .  | 306 |
| 4. Experiments with Free Atoms and Radicals . . . . .  | 314 |
| 5. Mechanism of the Oxygen-hydrogen Reaction. . . . .  | 321 |

|  |            |
|--|------------|
| <b>B. Carbon Monoxide Combustion . . . . .</b>   | <b>331</b> |
| 1. The Explosion Limits . . . . .  | 331        |
| 2. Reaction outside the Explosion Limits. . . . .  | 334        |
| 3. Spectroscopic Investigations of CO Combustion. CO Explosions in<br>the Presence of Nitrogen . . . . .                   | 336        |
| 4. The Mechanism of CO Combustion. . . . .   | 342        |
| <b>CHAPTER X: SPARK IGNITION II: REACTION IN ELECTRICAL DIS-<br/>CHARGES . . . . .</b>                                     | <b>346</b> |
| 1. Nature of Spark Discharge. Older Investigations on the Ignition<br>Properties of Various Sparks . . . . .               | 346        |
| 2. Finch's Investigations on the Reactions of Explosive Mixtures with<br>Discharges That Do Not Lead to Ignition . . . . . | 348        |
| 3. Experiments on the Ignition Properties of Various Sparks as Well as<br>of the Various Components of a Spark . . . . .   | 354        |
| 4. Other Observations on "Nonthermal" Ignition in Sparks and Dis-<br>charges . . . . .                                     | 359        |
| 5. Spark Ignition in the Engine . . . . .  | 360        |
| 6. Brewer's Investigations on Reactions as the Result of Discharges in<br>Nonexplosive and Explosive Mixtures . . . . .    | 361        |
| 7. Expressions for the Theory of "Nonthermal" Ignition in the Spark. .   | 362        |
| Appendix . . . . .   | 366        |
| <b>CHAPTER XI: THE COMBUSTION OF HYDROCARBONS: SURVEY OF THE<br/>FIELD . . . . .</b>                                       | <b>367</b> |
| <b>A. Combustion of Hydrocarbons in the Flame. . . . .</b>   | <b>369</b> |
| 1. Reaction Products in Explosion and Combustion . . . . .   | 370        |
| 2. Spectroscopic Observations. Reaction of Free Atoms and Radicals .   | 371        |
| 3. Flame Velocities . . . . .  | 375        |
| <b>B. The Slow Oxidation of Hydrocarbons . . . . .</b>   | <b>376</b> |
| 1. General Remarks . . . . .   | 376        |
| 2. The Kinetics of the Oxidation of Lower Aldehydes . . . . .  | 378        |
| 3. Decomposition of Carbohydrates, as Well as of Intermediate Products<br>of Combustion. Absorption Spectra . . . . .      | 394        |
| 4. The Oxidation of the Lowest Hydrocarbons (Acetylene, Ethylene,<br>Ethane, Propane). . . . .                             | 401        |
| 5. The Slow Oxidation of Further Hydrocarbon Compounds. Cold<br>Flames . . . . .   | 437        |
| <b>C. The Ignition of Hydrocarbons, Especially at Higher<br/>Pressures . . . . .</b>                                       | <b>471</b> |
| <b>D. The Theory of Hydrocarbon Oxidation . . . . .</b>  | <b>486</b> |

|  |            |
|--|------------|
| <b>CHAPTER XII: COMBUSTION IN OTTO ENGINES . . . . .</b>   | <b>501</b> |
| 1. Survey of the Observed Phenomena and Their Interpretation . . .   | 501        |
| 2. General Fundamentals and the Thermodynamics of Combustion in Engines. . . . .   | 503        |
| 3. The Knocking Process . . . . .  | 509        |
| 4. Essential Considerations in the Combustion and Knocking Processes in Engines. . . . .   | 525        |
| 5. Measurement of the Knocking Process . . . . .   | 535        |
| 6. Processes Preceding Knocking . . . . .  | 539        |
| 7. Investigations on Antiknock Substances . . . . .  | 547        |
| 8. Spectroscopic Investigations in Engines . . . . .   | 551        |
| 9. Knock Behavior and Chemical Constitution. Reaction-kinetic Equations . . . . .  | 553        |
| 10. Antiknock Substances . . . . .   | 567        |
| 11. Conclusions . . . . .  | 569        |
| <b>CHAPTER XIII: COMBUSTION IN THE DIESEL ENGINE. . . . .</b>  | <b>571</b> |
| 1. The Working Process of the Diesel Engine . . . . .  | 572        |
| 2. General Considerations Concerning the Combustion Process in Diesel Engines, Jet Injection, Evaporation, and Ignition. . . . . | 573        |
| 3. Practical Determination of Ignitibility of Diesel Fuels . . . . .   | 580        |
| 4. Reaction-kinetic Treatment of the Ignition Process in the Diesel Engine . . . . .   | 583        |
| 5. Further Reaction-kinetic Observations on Combustion in Diesel Engines . . . . .   | 588        |
| <i>General References . . . . .</i>  | <i>591</i> |
| <i>Name Index. . . . .</i>   | <i>595</i> |
| <i>Subject Index . . . . .</i>   | <i>603</i> |

## TABLE OF CONSTANTS

*For Conversion from the C.G.S. System to the F.P.S. System*

### Area

$$\text{sq cm} \times 0.155 = \text{sq in.}$$

$$\text{sq m} \times 10.76 = \text{sq ft}$$

### Energy

$$\text{gm cal} \times 0.00398 = \text{Btu}$$

$$\text{kg cal} \times 3.98 = \text{Btu}$$

$$\text{g cal/g mol} \times 1.8 = \text{Btu/lb mol}$$

$$\text{kg m} \times 7.23 = \text{ft lb}$$

### Length

$$\text{cm} \times 0.393 = \text{in.}$$

$$\text{cm} \times 0.0328 = \text{ft}$$

$$\text{m} \times 3.28 = \text{ft}$$

$$\text{km} \times 0.621 = \text{miles}$$

$$\text{\AA} \times 3.937 \times 10^{-9} = \text{in.}$$

### Pressure

$$\text{mm Hg} \times 0.0393 = \text{in. Hg}$$

$$\text{mm Hg} \times 0.0193 = \text{lb/sq in.}$$

$$\text{cm Hg} \times 0.393 = \text{in. Hg}$$

$$\text{atm} \times 14.69 = \text{lb/sq in.}$$

$$\text{kg/sq cm} \times 14.22 = \text{lb/sq in.}$$

$$\text{gram/sq cm} \times 0.01422 = \text{lb/sq in.}$$

### Temperature

$$1.8^{\circ}\text{C} + 32 = ^{\circ}\text{F}$$

$$1.8^{\circ}\text{K} (^{\circ}\text{C abs}) = ^{\circ}\text{R} (^{\circ}\text{F abs})$$

### Velocity

$$\text{cm/sec} \times 0.393 = \text{in./sec}$$

$$\text{cm/sec} \times 0.0328 = \text{ft/sec}$$

$$\text{m/sec} \times 3.28 = \text{ft/sec}$$

$$\text{km/sec} \times 3280 = \text{ft/sec}$$

### Volume

$$\text{cc} \times 0.061 = \text{cu in.}$$

$$\text{liters} \times 61 = \text{cu in.}$$

$$\text{liters} \times 1.056 = \text{qt}$$

$$\text{liters} \times 0.0353 = \text{cu ft}$$

$$\text{cu m} \times 35.3 = \text{cu ft}$$

### Weight

$$\text{grams} \times 0.0022 = \text{lb}$$

$$\text{kg} \times 2.20 = \text{lb}$$

$$\text{gram/cu cm} \times 62.4 = \text{lb/cu ft}$$





# EXPLOSION AND COMBUSTION PROCESSES IN GASES

## INTRODUCTION

By combustion, in the narrower sense, we generally mean the rapid reaction of oxidizable material with oxygen accompanied by the development of heat and usually the production of a flame. The oxidizable materials may be solid, liquid, or gaseous. The gaseous phase is the most important.<sup>1</sup> It is doubtful that combustion processes in this narrower sense are possible with liquid fuels. In processes involving liquid fuels, as in the case of Diesel engines, it is assumed that a considerable vaporization precedes combustion (the same applying, of course, to any wick lamp). If at the outset there is a ready mixture of combustible gas plus oxygen or air, the oxidation process can lead to an explosion, but it need not. The combustion processes of premixed gases do not differ from such other extremely exothermic gas reactions as the reaction of  $\text{Cl}_2 + \text{H}_2$ . In combustion processes in the narrower sense, insofar as premixed gases are concerned, we are always dealing with explosion processes. The combustion in a Bunsen flame, for example, is a stationary explosion.

We shall direct our interest chiefly to two groups of explosion phenomena, to wit:

A. Everything connected with the preliminary stages and the origin of an explosion (*e.g.*, explosion limits, ignition processes in auto-ignition, and other methods of ignition).

B. Everything dealing with the phenomena of the completed explosion (*e.g.*, the speed of propagation).

Auto-ignition processes include all those phenomena based upon the fact that, in an explosive mixture heated to an infinitesimal degree, the rate of reaction as the result of the infinitesimal change increases beyond all bounds.

The consideration of auto-ignition processes leads automatically to the study of the reaction preceding the actual explosion. In studying combustion processes in the narrower sense of the word, one is forced to draw into the discussion also those slower processes which are combustion processes only in the wider sense and are not (or not always) connected

<sup>1</sup> There is, of course, also the combustion of solids, *e.g.*, coal, but we shall not consider the latter in this discussion.

with the appearance of flames, since they are the slow reactions of the same materials or mixtures.

In the complete explosive reaction, the following will be of interest: what products of reaction appear, what temperatures are reached, what heat is liberated, and what radiation emanates. Because of the influence of dissociation at these high temperatures, the ordinary reaction formulas are inadequate for giving the products of reaction.

Beyond these general considerations, we are interested in the mechanism of the progress of an explosion, especially the speed with which an explosion started in one place is propagated to the unburned mixture. If the unburned gas is static, we are dealing with the so-called "ignition speed," or normal speed of combustion. The actual speed of combustion can, by the aid of currents, be much greater than the normal speed of combustion. If the speed of propagation of a combustion is very high, a shock wave may occur; in extreme cases, so-called "detonation" occurs, resulting from a combination of shock wave and chemical reaction.

The preceding applies to the combustion of premixed gases. In the case of gases not premixed or not sufficiently premixed, the speed of mixture must be added as a further determining element, as in the outer cone of the Bunsen flame, in the luminous flame, in the candle flame, and in the technical firing of nonpremixed gases (mixture by diffusion and also mixture by turbulence, as in the Siemens-Martin furnace).

The most important field of application of combustion processes is the internal-combustion engine. Not only the processes connected with ignition from outside sources (spark ignition) and flame spread, but equally the reactions taking place in hot fuel-air mixtures, are of interest in this connection. The latter are important for the ignition process in the Diesel engine as well as for the knocking process in the Otto engine. For this reason, we have also included a detailed treatment of the oxidation mechanism of hydrocarbons.

## CHAPTER I

### INITIAL STAGES OF EXPLOSIONS (AUTO-IGNITION) AS A THERMAL PHENOMENON

**1. Preliminary Remarks.**—The spontaneous development of explosions, or auto-ignition, is often a complicated process. However, we shall treat the processes leading up to it as simply as possible. We assume an exothermic and hence heat-producing reaction (endothermic reactions can never cause explosions) and direct our attention chiefly to the heating of the reaction mixture by means of the heat of reaction liberated. Thus we exclude those reactions in which the speed of reaction can increase considerably with time even at constant temperature (*cf.* Chap. VIII). Since in almost all reactions with rising temperature the speed of transformation increases, it is possible that, because heat is liberated by the initially slow reaction, the temperature (and therefore also the speed of reaction) will increase more and more, and explosion will finally result. This process of the origin of an explosion should be regarded as only an extreme case, but it is important and at the same time the simplest extreme case. For that reason, a detailed consideration of it is justified. Also, because it can be understood without going into the details of the course of the reaction, it will be discussed first.

The lowest temperature at which explosion occurs, under given conditions in a substance or a mixture, is generally designated as the "ignition temperature." From what has been said, it is clear that this temperature is not a constant for any given material.<sup>1</sup> The introduction of this concept is of great practical use, however, *e.g.*, in judging the danger of explosion in given mixtures, with the obvious reservation that one is conscious of the limits of the concept.

Even though the quantitative mathematical treatment of thermal explosion is only of relatively recent date, the fundamentals have been known for a long time. We owe it chiefly to van't Hoff,<sup>2</sup> whose definitions can be used even today:

"By ignition we mean not only the combustion phenomena, but any complete transformation that takes place as a result of a local rise in temperature up to the so-called ignition temperature."

<sup>1</sup> *Cf.* especially the numerical material in the supplement to this chapter.

<sup>2</sup> VAN'T HOFF, J.H., *Studies on Thermodynamics* (from "*Etudes de dynamique chimique*," 1884, reworked by E. Cohen), 1896; *cf.* especially pp. 141 and 145.

"In every phenomenon of this kind the following conditions are fulfilled:

"1. The change the ignition produces is accompanied by a development of heat.

"2. This change occurs more or less rapidly even below the ignition temperature.

"3. This change is accelerated by raising the temperature."

"The ignition temperature is that temperature at which the initial loss of heat (as a result of conduction, etc.) is equal to the heat the transformation simultaneously produces."

To be sure, branched chain explosions do not fit these definitions. They will be treated in Chap. VIII.

**2. Auto-ignition (Thermal Explosions).**—As already indicated, we intend to restrict our discussion in the following manner: we shall study an explosive mixture of gases enclosed in a container. In this mixture, a homogeneous gas reaction is to take its course. The wall of the container is considered to enable us to determine the initial temperature of the mixture. The heat loss to the wall must also be considered when the temperature of the gas rises above that of the surrounding wall.<sup>1</sup> The wall of the container is to play a role only insofar as it will enable us to determine on the one hand the initial temperature of the mixture and on the other hand that heat transmitted to the wall when, as a result of the reaction, the temperature of the gas mass rises above that of the containing wall. We shall leave out of consideration all finer distinctions, which play a part by effect of the wall on the course of the reaction and by the nature of the transformation as a chain reaction. Nevertheless, chain reactions are by no means to be excluded from this chapter.

We observe, then, the following process: Given a reaction chamber of the volume  $V$  and the experimental temperature  $T_0$ ; let the speed of reaction, perhaps related to the mol-number  $n$  of the end product, formed in the unit of volume, be

$$\frac{dn}{dt} = f(p) \exp\left(-\frac{E}{RT}\right) \quad (1)$$

where, in a reaction of the second order, in which the concentrations of both components are proportional to the total pressure  $p$ , the following equation is especially applicable:

$$f(p) \cong \beta p^2 \quad (2)$$

If the released heat of reaction per mol of transformation is  $Q$  (we must of course assume that we are dealing with an exothermic reaction), then in the unit of time the quantity of heat to be released in the reaction

<sup>1</sup> The assumption is made that heat loss from the containing wall to the outside is so rapid that its temperature can be regarded as constant.

volume  $V$  is

$$\frac{dq_1}{dt} = Q \frac{dn}{dt} V = QVf(p) \exp\left(-\frac{E}{RT}\right) \quad (3)$$

The heat set free is partly used to heat the gas mixture and partly given off to the vessel wall held at constant temperature. Moreover, it is reasonable to assume that the quantity of heat given off to the wall is approximately proportional to the excess of the gas temperature  $T$  over the wall temperature  $T_0$ , in other words, to write for the quantity of heat given off in the time unit

$$\frac{dq_2}{dt} = A(T - T_0) \quad (4)$$

In addition it must be noted:

1. The quantity  $A$  will depend on the form as well as on the dimensions of the container. It will, among other things, be about proportional to the surface. In addition, it also depends on the thermal conductivity of the gas mixture and therefore indirectly on the temperature. The latter dependence will be disregarded from now on because of the approximate character of the calculations. This is to be considered in judging the accuracy of the results.

2. The gas mixture will naturally not adopt a strictly constant temperature  $T$ . Rather a temperature gradient will prevail from the interior to the edge. By the temperature  $T$  in (4) there is to be understood an average value suitably determined from the spatially variable temperature of the gas mixture.

Under these assumptions, we shall now examine what happens when an explosion occurs. Qualitatively this has been known since van't Hoff.<sup>1</sup> If (Fig. 1) we plot the heat produced in a unit of time ( $dq_1/dt$ ) against the temperature, the path shown will result according to (3). A heating of the gas mixture can take place only as long as the heat produced is greater than that given off. If the latter ( $dq_2/dt$ ) is given according to (4) by the straight line in Fig. 1, the mixture can heat up only to the temperature  $T_1$ . Above this temperature, the heat given off would exceed the heat produced. If, however, by reason of a different choice of experimental conditions, *e.g.*, the use of a larger reaction vessel, the heat given off per unit of time were given by the dotted line, more heat would constantly be produced than was given off. Accordingly, the temperature in the reaction vessel would grow beyond all bounds, and an explosion would result.<sup>2</sup>

<sup>1</sup> VAN'T HOFF, J. H., "Etudes de dynamique chimique," 1884.

<sup>2</sup> As long as one disregards the reduction of concentration of the end products as a result of the transformation, which finally causes the speed of reaction to be reduced.

In the following, we shall be guided by the presentation of Semenov,<sup>1</sup> who was the first to formulate the conditions necessary for the appearance of an explosion quantitatively in connection with the situation prevailing in Fig. 1.<sup>2</sup> We present the processes once more in a graph in Fig. 2. At a constant gas temperature  $T_0$  and a constant mixture proportion, the heat lost by conduction is shown by the straight line  $I$ , even when the pressure in the reaction vessel varies (up to corrections conditioned by varying convection), since the heat conductivity of a gas is independent of the pressure, except for very small pressures that do not come into consideration here. If the proportions of the mixture are changed,

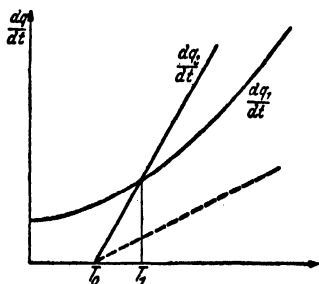


FIG. 1.—Heat given off ( $dq_2/dt$ ) and heat produced ( $dq_1/dt$ ) in an exothermic reaction.

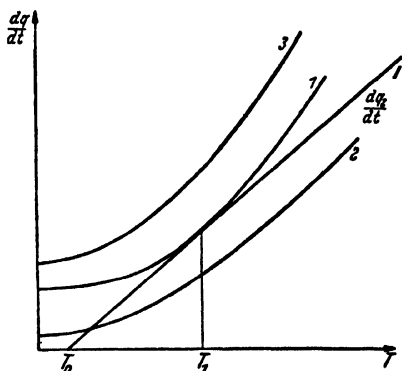


FIG. 2.—Treatment of thermal explosion according to Semenov. Heat produced (1, 2, 3) and heat given off,  $I$ .

the direction of the straight lines will change too—a fact that will not be taken into account here but should be considered occasionally in practice.

For the heat produced, three different curves are given in Fig. 2. They belong to the same mixture but to different pressures. In contrast to the heat lost by conduction, the heat liberated has higher values as the pressure increases; and here the more exact law according to which the production of heat depends on the pressure is expressed by the equation of the speed of reaction. Under our special assumptions (1), (2), and (3),  $dq_1/dt$  would be proportional to  $p^2$ .

One can see from Fig. 2 that under the conditions of curve 2 no explosion can result, but rather that a gas temperature slightly higher than the outer temperature  $T_0$  would result. In curve 3, auto-ignition would certainly take place, since more heat is constantly produced than

<sup>1</sup> SEMENOFF, N., *Z. Physik*, **48**, 571 (1928); cf. Also "Chemical Kinetics and Chain Reactions," Oxford, 1935.

<sup>2</sup> A corresponding graph has been discussed by Taffanel and Le Floche [*Compt rend.*, **156**, 1544; **157**, 496, 714 (1913)].

is lost by conduction. Curve 1 represents that borderline case in which the curve and the straight line meet and in which at the point of contact at  $T_1$  an unstable equilibrium would exist between heat production and heat loss; by a small addition of energy from the outside, the unstable condition must change into explosion. Mathematical principles must give us the law for the critical limits of explosion. By critical limits of explosion, we mean either the temperature above which, at constant pressure, auto-ignition sets in (temperature of ignition) or the pressure above which, at constant temperature, explosion takes place.

Curve 1 is obviously characterized by the fact that, for  $T = T_1$ ,  $dq_1/dt = dq_2/dt$  and their derivations according to temperature are equal. In other words,

$$\left(\frac{dq_1}{dt}\right)_{T=T_1} = \left(\frac{dq_2}{dt}\right)_{T=T_1} \quad (5)$$

and

$$\left(\frac{\partial}{\partial T} \frac{dq_1}{dt}\right)_{T=T_1} = \left(\frac{\partial}{\partial T} \frac{dq_2}{dt}\right)_{T=T_1} \quad (6)$$

If we substitute for  $dq_1/dt$  and  $dq_2/dt$  the values from (3) and (4), we get

$$QVf \exp\left(-\frac{E}{RT_1}\right) = A(T_1 - T_0) \quad (5a)$$

$$\frac{E}{RT_1^2} QVf \exp\left(-\frac{E}{RT_1}\right) = A \quad (5b)$$

From this, by means of division,

$$\frac{RT_1^2}{E} = T_1 - T_0 \quad (7)$$

and, by substitution in (5a),

$$QVf \exp\left(-\frac{E}{RT_1}\right) = A \frac{RT_1^2}{E} \quad (8)$$

From (7), we get the rise in temperature of the gas  $T_1 - T_0$  under the critical conditions. In order to gain a comprehensive view, let us substitute the following approximate values as they correspond to actual conditions in oxidation reactions within the range:  $T_0 \cong 500^\circ$  to  $1000^\circ$  abs;  $E \cong 50,000$  cal;  $R = 2$  cal/deg.

First of all, (7) leads to

$$T_1 = \frac{E}{2R} \pm \sqrt{-\frac{T_0 E}{R} + \frac{E^2}{4R^2}} \quad (9)$$

Since the solution cannot yield a ridiculously high temperature, as would be the case with the plus sign and substitution, it must be clear that

$$T_1 = \frac{E}{2R} - \sqrt{-\frac{T_0 E}{R} + \frac{E^2}{4R^2}} \quad (10)$$



If we assume that  $T_0$  is small compared with  $E/R$  according to the values indicated, we get, by development including terms up to terms of the second order in  $R/E$ ,

$$\begin{aligned} T_1 &= \frac{E}{2R} - \frac{E}{2R} \sqrt{1 - \frac{T_0 4R}{E}} \\ &\cong \frac{E}{2R} - \frac{E}{2R} \left( 1 - \frac{2RT_0}{E} - \frac{2R^2 T_0^2}{E^2} \right) = T_0 + \frac{T_0^2 R}{E} \end{aligned} \quad (11)$$

or

$$T_1 - T_0 \cong \frac{RT_0^2}{E} \quad (12)$$

a result that would also have been achieved directly from (7) by the substitution of  $T_0$  for  $T_1$  on the left-hand side.

If we now proceed to (5a), first of all

$$QVf \exp \left\{ -E \left[ RT_0 \left( 1 + \frac{RT_0}{E} \right) \right] \right\} = A \frac{RT_0^2}{E} \quad (13)$$

Since (cf. page 7)  $RT_0/E \ll 1$ , we get the following approximation:

$$\frac{1}{1 + \frac{RT_0}{E}} \cong 1 - \frac{RT_0}{E}$$

and thus

$$QVf \exp \left[ -\frac{E}{RT_0} \left( 1 - \frac{RT_0}{E} \right) \right] = eQVf \exp \left( -\frac{E}{RT_0} \right) = A \frac{RT_0^2}{E} \quad (14)$$

Employing logarithms results in

$$\ln eQVf - \frac{E}{RT_0} = \ln \frac{AR}{E} + 2 \ln T_0 \quad (15)$$

We now limit this by introducing, according to (2),  $f = \beta p^2$ , in other words by assuming a bimolecular reaction. Accordingly

$$\ln eQV\beta + 2 \ln p - \frac{E}{RT_0} = \ln \frac{AR}{E} + 2 \ln T_0 \quad (16)$$

or

$$\ln \left( \frac{p_{cr}}{T_0} \right) = \frac{E}{2RT_0} - \frac{1}{2} \ln \frac{eQV\beta E}{AR} = \frac{E}{2RT_0} + \text{const} \quad (17)$$

Equation (17) is the condition for the appearance of thermal explosion deduced by Semenov;<sup>1</sup> it represents a relation between the critical pressure of explosion  $p_{cr}$ , the temperature of the container  $T_0$ , and the heat of activation of the reaction  $E$ . The greater the pressure, the lower the temperature at which the mixture explodes (*i.e.*, ignites).

<sup>1</sup> Without the limitations given above; cf. pp. 14ff.

It should be pointed out that the above-mentioned suppositions were necessary for deducing this equation, and particularly that the limitation is for a reaction of the second order,  $f \sim p^2$ . For reactions of other orders, the equation would have to be modified (*cf.* page 16). If these suppositions are fulfilled and if the critical pressures of explosion dependent on the temperature have been determined, then plotting  $\log p_{cr}/T_0$  against  $1/T_0$  must yield a straight line. From the slope of these straight lines, the heat of activation of the reaction  $E$  may be determined.

We shall see later that thermal explosion is not the only way in which an explosion can develop and that, for the other borderline case, the explosion by chain-branching, a relation similar to (17) can be deduced. One must therefore not conclude from the form of the observed relation that according to (17) one is dealing with a thermal explosion. Rather, it is necessary to make a detailed analysis of the conditions.

The following will demonstrate at this point that thermal explosion is not the only possible mechanism. All previous considerations were based on the unexpressed supposition that all the energy liberated during the transformation is present as heat. "To be liberated as heat" means that the energy is divided among all degrees of freedom of the system in a manner corresponding to the equilibrium temperature of the moment. This supposition, which perhaps sounds self-evident at first, need not necessarily be fulfilled. The attainment of the equilibrium temperature in the gas is a process that demands a definite, though perhaps brief, time.<sup>1</sup> But if the energy being liberated during the reaction should appear as activation energy of individual particles of relatively long duration (let us say in the form of free atoms or radicals, which can hasten the reaction themselves, without a rise in temperature on the part of the gas as a whole), then all calculations given above are invalid. It is precisely with such cases that we shall have to deal in Chap. VIII.

It can be considered a sufficient test for the presence of a pure thermal explosion if the mechanism of the nonexplosive reactions and their temperature coefficient have been determined and if this temperature coefficient (in the case of a bimolecular reaction) coincides with the value calculated from (17). Particularly, if it has been found that no chain reaction is present, one can be sure that one is dealing with a pure thermal explosion. Thermal explosion can, however, also appear in chain reactions. It would be well in such cases to make sure by direct measurement of the rise in temperature before the explosion that the rise in temperature and not chain-branching was the cause of explosion.

The cases of definitely established thermal explosions are relatively

<sup>1</sup> Cf. BERGMANN, L., "Der Ultraschall" (The Ultra-sound), Berlin, 1937.

rare, although it is to be assumed that, at least under certain conditions, this process is quite frequent.

A direct test establishing the presence of a thermal explosion by direct temperature measurements in a reaction mixture has been successful in only a few cases thus far, *e.g.*, in the study of the decomposition of azomethane (Allen and Rice<sup>1</sup>), as well as in the decomposition of ethyl azide (Campbell and Rice<sup>2</sup>). In these examples, a chain mechanism seems less likely by the very nature of the transformations.

Rice and his associates have also analyzed in greater detail the time factor of a thermal explosion and have compared the results with the times of induction found in the experiments (or conversely have computed

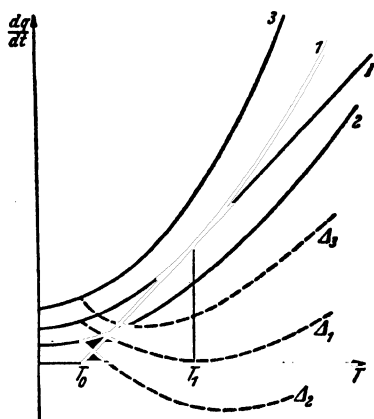


FIG. 3.—Same as Fig. 2. Added are the curves  $\Delta_1$ ,  $\Delta_2$ , and  $\Delta_3$ , which indicate how much more heat is developed in a unit of time than is given off.

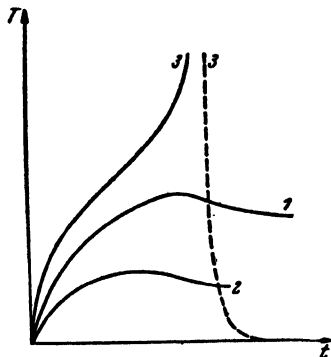


FIG. 4.—Temporal course of the temperature in cases 1, 2, and 3, as given in Fig. 3.

heats of reaction from them). From what appears in Fig. 2 and in a modified form is repeated in Fig. 3, the following is clear: in addition to the curves for heat generated (1, 2, 3) and heat given off (straight line  $I$ ), Fig. 3 also gives as differences the curves  $\Delta_1$ ,  $\Delta_2$ ,  $\Delta_3$ , respectively, to plot the difference between the heat produced and the heat given off. The heating velocity of the mixture will be proportional to this difference at every temperature. In Case 1, the temperature would rise only to  $T_1$  and would then become constant. But if, by a minute disturbance, it should go beyond  $T_1$ , it would then rise by itself without limit<sup>3</sup> (at least as long as the consumption of the initial materials is disregarded).

<sup>1</sup> ALLEN, A.O., and O.K. RICE, *J. A. Chem. Soc.*, **57**, 310 (1935).

<sup>2</sup> CAMPBELL, H.C., and O.K. RICE, *J. Am. Chem. Soc.*, **57**, 1044 (1935).

<sup>3</sup> As we shall see later, the temperature in Case 1 would have to fall again, since with increasing transformation at constant temperature the reaction velocity must decrease. Up to this point, we have disregarded this fact because we were always dealing only with a brief initial period.

In Case 3,  $T$  will never be stationary, since  $\Delta$  always remains finite and positive. Since, however,  $\Delta$ , also traverses a minimum, the velocity of the rise in temperature will traverse a minimum also in Case 3; or, if temperature is plotted against time, the corresponding curve will show a turning point. The change of temperature in relation to time is therefore given graphically for Cases 1, 2, and 3 in Fig. 4. Thus the final decrease of the reaction velocity as the result of the consumption of the initial materials is taken into account. In Case 3, the curve would also have to pass finally through a maximum, since with increasing transformation the reaction velocity will finally diminish again.

What has been presented qualitatively in Fig. 4 constitutes a study by Rice, Allen, and Campbell.<sup>1</sup> Using our former symbols [Eqs. (3) and (4)], the excess of the heat liberated in a unit of time over that given off becomes

$$\frac{dq}{dt} = \frac{dq_1}{dt} - \frac{dq_2}{dt} = QVf \exp\left(-\frac{E}{RT}\right) - A(T - T_0) \quad (18)$$

In order that the equation will be valid beyond the very first stage, the variability of the concentrations must be taken into account, for which we introduce at this point (following Rice) an exponential relation corresponding to a monomolecular reaction

$$f \sim n = n_0 e^{-kt} \quad (19)$$

in which  $k$  again depends on the temperature exponentially according to (1), a fact that materially complicates the integration.<sup>2</sup> If one divides the average heat capacity<sup>3</sup> of the mixture by  $n_0 V c_v$  in order to proceed from heat energy to temperature change, (18) becomes

$$\frac{dq/dt}{n_0 V c_v} = \frac{dT}{dt} = \frac{Q}{c_v} \exp\left(-\frac{E}{RT}\right) e^{-kt} - \frac{A}{n_0 V c_v} (T - T_0) \quad (20)$$

This is the differential equation from which Rice and his associates proceed. Numerically it can be integrated only with great difficulty, a task that Rice and his associates have undertaken for a number of parameters. Qualitatively a group of curves such as those given in Fig. 4 result. We can give no further details because of lack of space. The same authors also give approximation methods for the treatment of the problem with which we cannot deal in detail here either. We wish merely to mention that they permit the determination of the heat of reaction

<sup>1</sup> RICE, O.K., A.O. ALLEN, and H.C. CAMPBELL, *J. Am. Chem. Soc.*, **57**, 2212 (1935).

<sup>2</sup> Since the experiments of Rice deal with an exothermic monomolecular reaction leading to an explosion, this relation is justified.

<sup>3</sup>  $c_v$  is the mol specific heat per mol of the reaction mixture.

from individual explosion experiments (instead of from the maximum pressure) and that the agreement of the values obtained from a series of experiments permits conclusions about the suppositions made regarding the presence of a thermal explosion. In the case of reactions of azo-methane and ethyl azide, these facts also corroborate the existence of a thermal explosion.

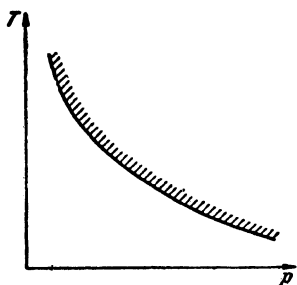


FIG. 5.—Explosion limit in thermal explosion (explosion on the shaded side).

Later we shall enlarge briefly on the more general treatment of the equations for thermal explosions, but we wish to include several other remarks on the subject at this point.

The relation deduced for the critical limit of explosion in Eq. (17) is given qualitatively in Fig. 5. The shaded portion of the curve on the right side (Fig. 5) corresponds to the region in which explosion takes place [this is also true qualitatively, if one does not introduce the limitation in respect to reactions of the second order, as contained in Eq. (17), and only if the order of the reaction is  $> 0$ ]. It is, to be sure, a general observation that such a critical limit of pressure exists, but a course of reaction such as is given in Fig. 6, or better in Fig. 7, is frequently found also. In Fig. 6, only the section of the curve  $AB$  could correspond to a thermal explosion, whereas the absence of the explosion above a certain pressure, curve  $BC$ , must, from the standpoint of the theory of heat and without further assumptions (such as specific wall influences), remain

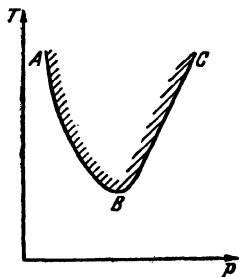


FIG. 6.

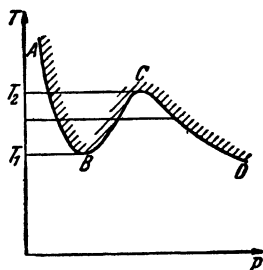


FIG. 7.

FIGS. 6 AND 7.—Observed explosion limits that cannot be interpreted as thermal explosion.

completely incomprehensible. In Fig. 7, one could assume that the section  $CD$  of the curve would correspond to a thermal explosion, but the two additional limits of pressure appearing between  $T_1$  and  $T_2$  (branches  $AB$  and  $BC$ ) could not be understood in this manner. Further details on this matter will be given in Chap. VIII.

As far as the terms are concerned, it should be kept in mind that the term "limit of explosion" is used throughout the literature in a double

sense. It is used first—and on this meaning the observations thus far have been based—as the limit of pressure below or above which, in a mixture of a given composition, at a given temperature, explosion of itself just fails to occur. The term is also used as limits of composition outside of which an explosion, by external ignition, in a mixture of given pressure (usually atmospheric pressure) and given temperature (usually room temperature), cannot propagate. If one speaks only of upper or lower limits of explosion, one generally means, especially in the technical literature, the limits of the composition of the mixture for external ignition. It would perhaps be advisable to differentiate both concepts by speaking of critical pressure limits for spontaneous explosion, and of critical composition (mixture) limits for external ignition, or rather of ignition limits. The critical mixture limit will of course also depend in general on the temperature and pressure; higher temperature or higher pressure will in general, but not always, hasten explosion and therefore extend the critical range.

Insofar as these conditions are to be interpreted purely on the basis of the theory of heat, it can be seen from the foregoing that all such entities will depend on the method employed (*e.g.*, in all cases the conduction of heat depends on the dimensions of the container) and that they therefore cannot be characteristic constants for the fuel alone. In addition, it must be noted that, in determining the critical mixture limits by means of external ignition (ignition by sparks, flames, etc.), it is a matter not only of whether an explosion can take place at all in the mixture in question, but in addition of whether an explosion induced at one place propagates to the unburned mixture. Practically, therefore, problems of the propagation of the flame will always play an essential role. These will be treated in greater detail in Chap. III.

Even though it is useless to establish the ignition temperatures and explosion limits characteristic of the individual fuel independent of external conditions, a considerable technical interest nevertheless exists in determining the ignitibility of gas mixtures for conditions that actually occur, whether producing the ignition is important—as in the gas and gasoline engine, the gas burner, etc.—or whether on the contrary its avoidance is important, as in various explosive mixtures in the atmosphere. There is, then, a practical reason for defining and determining the above-mentioned entities for these special conditions, as long as the surrounding conditions have been determined accurately. A general review of the experimental methods for determining the ignition temperatures and the results achieved appears at the end of this chapter.

Even though, as has been mentioned, by no means is every explosion caused by a rise in temperature, every explosion must (even if it began to develop exothermally as a chain explosion) change over finally to

the type of the above-described heat explosions, as soon as the reaction velocity, and hence the production of heat, has exceeded a certain limiting value. We shall have to use this later (Chap. VIII) in defining explosions.

For the suppression of explosions, we can draw the following practical conclusions: according to the theory of heat, an addition of inert gases, which increases the heat capacity, must tend to reduce the reaction velocity (*e.g.*, carbonic acid with high specific heat). Further, an addition of gases of high normal thermal conductivity (helium) can increase the conduction and thus reduce the inclination toward autoignition.

The conditions for thermal explosion given above could also be applied to the case of heterogeneous mixtures, *e.g.*, coal dust in air or the processes in the Diesel engine, *i.e.*, fuel fog in air. Only the function that gives the dependence of the velocity of reaction on pressure, concentration, and temperature would thereby become more complicated. Then—as, for instance, in the case of coal dust—the phase-limit reaction would enter in; whereas in Diesel combustion the heat-producing reaction would occur mainly in the gas phase, but the vaporization process of the drops would have to be considered as a heat-consuming transformation codetermining the velocity (*cf.* Chap. XIII).

**3. Detailed Discussion of the Explosion Equations.**—In the following, we shall treat a number of special cases of thermal explosion in connection with the work by Todes.<sup>1</sup> The calculations of Todes are, to be sure, only approximate (in no other way is an evaluation in a general form possible). Since the equations can easily be generalized and since they can be integrated more accurately in the individual case by means of numerical methods, they may be of service as a point of departure also for more exact calculations in important practical cases.

We proceed from our Eq. (18)

$$c_v V n_0 \frac{dT}{dt} = \frac{dq}{dt} = QVf \exp\left(-\frac{E}{RT}\right) - A(T - T_0) \quad (18)$$

which we shall transcribe to the extent of introducing a more general expression<sup>2</sup> for the reaction velocity  $f \exp(-E/RT)$

$$- \frac{dn}{dt} = k n_0 F\left(\frac{n}{n_0}\right) \exp\left(-\frac{E}{RT}\right) \quad (21)$$

where  $F(n/n_0)$  is any function of the percentile transformation, which, especially for reactions of the first, second order, etc., goes over into  $n/n_0$ ,  $(n/n_0)^2$ , etc.;  $k$  is not the real constant of velocity, but  $k = k' n_0^{\nu-1}$ , if  $\nu$  is the order of the reaction, and  $k$  is therefore constant only during an experiment (in a more general case, the concentrations of the various reagents would have to be introduced).

We introduce with Todes the dimensionless variables

$$\xi = \frac{n}{n_0} \quad \Theta = \frac{T}{T_0} \quad \tau = kt \quad (22)$$

<sup>1</sup> Todes, O.M., *Acta Physicochim. URSS*, **5**, 785 (1936). *Cf.* also APPIN, A., J. CHARITON, and O. Todes, *Acta Physicochim. URSS*, **5**, 655 (1936).

<sup>2</sup>  $n$  here designates the concentration of the initial products.

and the dimensionless constants

$$\alpha = \frac{E}{RT_0} \quad \lambda = \frac{Q}{c_v T_0} \quad \mu = \frac{A}{c_v n_0 V k} = \frac{1}{\tau_c} \quad e^{-\alpha} = (v_0 -) \frac{1}{\tau_r} \quad (23)$$

$\lambda$  is the "relative heat effect," in other words, the maximum rise in temperature, related to the absolute initial temperature  $\lambda = (T_m - T_0)/T_0$ , where  $T_m$  is the maximum temperature reached in adiabatic combustion assuming constant thermal capacity ( $\lambda$  normally lies between 1 and something over 10);  $\tau_c$  is the reduced (dimensionless) thermal relaxing time (*i.e.*, the reduced time in which the temperature difference  $T - T_0$  would sink to  $1/e$  of its amount by conduction);  $\tau_r$  correspondingly is the "reaction time."

By means of the abbreviations (22) and (23), one gets, for the reduced reaction velocity,

$$-\frac{d\xi}{d\tau} = F(\xi)e^{-\alpha/\Theta} \quad (24)$$

and, for the reduced velocity of heating,

$$\frac{d\Theta}{d\tau} = \lambda F(\xi)e^{-\alpha/\Theta} - \mu(\Theta - 1) \quad (25)$$

Equation (25) therefore corresponds to Eq. (20) of Rice and associates. For the conditions of the work of these authors, the investigations of Todes offer nothing new. On the contrary, Todes does not give solutions of such a general nature that they would be equivalent to numerical integrations of Rice. The importance of Todes's work lies rather in the fact that it furnishes the course of transformation for a series of special cases interesting from a technical point of view. These are to be discussed now.

*a. Reaction of the "Zero Order."*—The assumption of a reaction of the zero order, *i.e.*, a reaction velocity independent of the concentration, is justified when the explosion develops in so short a time that the initial concentration has not yet noticeably seduced. For this purpose, Eqs. (24) and (25) simplify to

$$-\frac{d\xi}{d\tau} = e^{-\alpha/\Theta} \quad (26a)$$

and

$$\frac{d\Theta}{d\tau} = \lambda e^{-\alpha/\Theta} - \mu(\Theta - 1) \quad (26b)$$

Under variable pressure,  $\alpha$  and  $\lambda$  remain unchanged, while the "relative loss of heat" [which according to (23) is proportional to  $1/(n_0 k)$ ] is reduced with rising pressure.

As discussed earlier (Figs. 1 and 2), depending on the value of  $\mu$ , the heat production constantly exceeds the loss, or, at a slightly higher temperature, equilibrium is reached.

The conditions for explosion formulated earlier can now be written

$$\lambda e^{-\alpha/\Theta_k} = \mu(\Theta_k - 1) \quad \frac{d}{d\Theta} (\lambda e^{-\alpha/\Theta}) = \frac{d}{d\Theta} [\mu(\Theta - 1)]_k \quad (27)$$

For the critical temperature of explosion  $\Theta_k^*$  we obtain from this the quadratic equation corresponding to (12)

$$\Theta_k^2 - \alpha(\Theta_k - 1) = 0 \quad (28)$$

\*  $\Theta_k$  corresponds not to the earlier  $T_0$  but to  $T_1$  on p. 7.



and from this

$$\Theta_k = \frac{\alpha}{2} - \sqrt{\frac{\alpha^2}{4} - \alpha} \cong 1 + \frac{1}{\alpha} + \frac{2}{\alpha^2} \dots \quad (29)$$

and thus the first equation (27)

$$\mu_k = \frac{\lambda e^{-\alpha/\Theta_k}}{\Theta_k - 1} \cong \lambda \alpha e^{-\alpha} \left(1 - \frac{1}{\alpha} \dots\right) \quad (30)$$

According to Semenov, we obtain the generalized condition for explosion if we put with (23)\*

$$A \sim \frac{\text{surface of container}}{\text{diameter of container}} \cdot \text{diameter of container} = d \quad (31)$$

and

$$n_0 k \cong \left(\frac{p_0}{T_0}\right)^{\nu} f(\gamma) \dagger \quad (32)$$

since the velocity in a reaction of the  $\nu$ th order is proportional to the  $\nu$ th power of the concentration, which on its part is again proportional to  $p/T$ , while  $f(\gamma)$  is a function of the relative gas composition. The assumption (32) does not contradict the presupposition of a reaction of zero order introduced above, for this merely states that the expression (32) is kept constant in the observed reaction. More problematic is the assumption (31), which can probably be fulfilled only roughly. Thus one obtains from (30)

$$\mu k \sim \frac{T_0^{\nu}}{d^2 p_k^{\nu} f(\gamma)} \text{ proportional } \frac{1}{T_0^2} e^{-E/RT_0} \quad (33)$$

and by utilizing logarithms

$$\ln \frac{p_k}{T_0} = \frac{1}{\nu} \frac{E}{RT_0} + \frac{2}{\nu} \ln T_0 + \text{const} \quad (34)$$

In addition, there follows from (33) for constant  $T_0$  and  $f(\gamma)$  as a condition for the dependence of the critical pressure on the diameter of the container

$$p_k^{\nu} d^2 = \text{const} \quad (35)$$

a relation that is only approximate and in a formally similar manner can also be obtained in chain explosions.

*b. Near Isothermal Reactions.*—If the relative conduction of heat is great compared with the critical conduction leading to explosion, if, therefore,

$$\mu \gg \mu_k = \alpha \lambda e \mu^{-\alpha} \quad (36)$$

the Eqs. (26) can be approximately integrated, because then also  $\Theta - 1$  must be of a small magnitude and, by developing the exponential function according to powers of  $(\Theta - 1)$  from (26b), we get

$$\frac{d\Theta}{d\tau} = \lambda e^{-\alpha} - (\mu - \alpha \lambda e^{-\alpha})(\Theta - 1) \quad (37)$$

\* The amount of heat given off to the wall will be proportional to its size and to the drop in temperature. The latter will be approximately inversely proportional to  $d$ . Todes makes a different attack, which is not correct, however.

† The dependence on temperature is not exact, since that of the number of collisions has not been taken into account.

which, integrated, yields (again under the assumption of a reaction of zero order, i.e., coefficients independent of  $\tau$ , in other words, for a small transformation)

$$\Theta = 1 + \frac{\lambda e^{-\alpha}}{\mu - \alpha \lambda e^{-\alpha}} \left[ 1 - e^{-(\mu - \alpha \lambda e^{-\alpha})\tau} \right] \quad (38)$$

$\Theta$  therefore trends asymptotically toward the maximum value (so that we use the fact that  $\alpha$  in general is large compared with 1)

$$\Theta_s \cong 1 + \frac{\lambda e^{-\alpha}}{\mu} \left( \text{exactly} = 1 - \frac{\lambda e^{-\alpha}}{\mu - \alpha \lambda e^{-\alpha}} \right) \quad (39)$$

$\Theta$  follows exactly from the maximum condition deduced from (26b)

$$\frac{d\Theta}{d\tau} = 0 = \lambda e^{-\alpha/\Theta_s} - \mu(\Theta_s - 1) \quad (40)$$

For the given value of  $\alpha$ , the maximum temperatures  $\Theta_s$  dependent on  $\lambda/\mu$  are given by a curve like that given in Fig. 8. For  $\lambda/\mu$  values above  $\lambda/\mu_k$ , there is no longer a

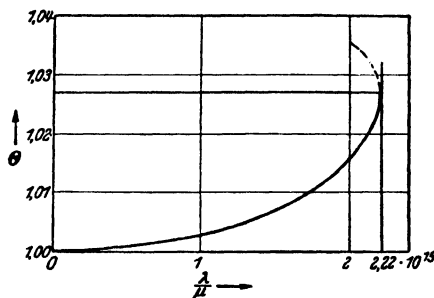


FIG. 8.—Reduced maximum temperature  $\Theta$  at almost isothermic reaction, for  $\alpha = 40$ . (From Todes.)

fixed temperature  $\Theta_s$ , a situation demanded also by our earlier remarks. It is noteworthy that, in the example cited, the highest fixed temperature possible lies only around 2.7 above the initial temperature (which is also the same order of magnitude as the temperature rises measured by Rice and his associates). This shows once more that the very first initial stage is the determining factor for the development of the explosion.

*c. Adiabatic and Near Adiabatic Explosion; Induction Period.*—In adiabatic cases, the relative heat conduction  $\mu$  in (26b) is to be disregarded, and one obtains

$$\frac{d\Theta}{d\tau} = \lambda e^{-\alpha/\Theta} \quad (41)$$

As a solution, one finds

$$\lambda\tau = [\alpha Ei(\alpha) - e^\alpha] - \left[ \alpha Ei\left(\frac{\alpha}{\Theta}\right) - \Theta e^{\alpha/\Theta} \right] \quad (42)$$

in which  $Ei$  is the exponential integral:<sup>1</sup>

$$Ei(x) = \int_{\infty}^{-x} \frac{e^{-u} du}{u} \quad (43)$$

<sup>1</sup> Tabulated, for example, by Jahnke-Emde, "Tables of Functions."

For  $[x] > 17$ , the asymptotic development holds

$$Ei(x) \cong \frac{e^x}{x} \left( 1 + \frac{1!}{x} + \frac{2!}{x^2} + \frac{3!}{x^3} + \dots \right) \quad (44)$$

from which it is clear that for most of the values in question from  $\alpha (> 20)$  through the order of magnitudes of  $\tau\lambda$  is given by the first member in (42) [the second is about  $1/e$  of the first, in case  $\Theta \cong 1 + (1/\alpha)$ ]. An increase of the temperature  $\Theta$  to about  $\sim 1 + (1/\alpha)$ , results in an induction period of the order of magnitude

$$\tau_i \cong \frac{1}{\lambda} [\alpha Ei(\alpha) - e^\alpha] \cong \frac{e^\alpha}{\alpha\lambda} \left( 1 + \frac{2!}{\alpha} + \dots \right) \quad (45)$$

By using (22) and (23), the induction period  $t_i$  becomes

$$t_i = \frac{e^{E/RT_0} R T_0^2 c_0}{kEQ}$$

The remaining temperature increase takes place then in an extraordinarily short time (Fig. 9).

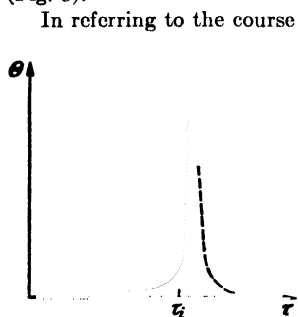


FIG. 9.—Temporal course of the temperature (reduced magnitudes) in adiabatic explosion; induction period  $t_i$ . (From Todes.)

In referring to the course of the curve in Fig. 9, it must be remembered that, in contrast to the earlier treatment according to Rice, heat conduction as well as the decrease in reaction velocity caused by the decrease in the concentrations is disregarded. Neglecting the heat conduction causes the disappearance of the turning point in the heating curve.

Todes corrects the calculation somewhat by taking into account low heat conduction and sets up also in this case an approximate relation for the induction period. As a maximum period, he obtains the 1.7 fold of the induction period in adiabatic cases. (This extrapolation is probably not very important.) It is again noteworthy that, for the transformation during the induction period, one obtains only an order of magnitude of 1 per cent of the total transformation.

*d. Forced Ignition.*—By forced ignition, Todes understands ignition caused by the creation of initial centers of reaction by other than thermal means, *e.g.*, by lighting. When this is possible, one is normally dealing with chain reactions. Nevertheless, the case dealt with by Todes is different from so-called "chain explosions," in which the branching of the chains, without a rise in temperature and independent of the initial concentration of the active centers, leads to explosion. Here, however, although we may be dealing with a chain reaction, the heat production dependent on the initial concentration of the active centers causes the explosion. On account of details of calculation, which, by the way, seem to need correction, we refer the reader to Todes.

Since, in spark ignition, one is not dealing with chain explosions the conditions of the above-discussed case might prevail within the spark. This will be discussed later

*e. Ignition by Adiabatic Compression.*—Ignition by adiabatic compression is different from ignition by heating the gas in a closed container in the following way. In adiabatic compression, the gas generally reaches a perceptible reaction velocity only at temperatures considerably above those of the wall, since the wall, in contrast to the other case, is not heated too. As a result, there will always be a relatively much

greater conduction of heat from the gas to the wall than when the whole container is heated. Although, during the heating of the container to temperatures not sufficient for explosion, the gas temperature must always rise a little before it becomes fixed, the temperature in adiabatic condensation that does not lead to explosion can drop, but to a stationary value still above the wall temperature. Heat production ( $dq_1/dt$ ) and heat conduction ( $dq_2/dt$ ) will be given by two curves, as in Fig. 10 (with the same approximation as before). Only with very slight compression for temperatures under  $T_s$  will the reaction temperature rise to the stationary terminal value  $T_s$  as the result of self-heating of the mixture. In temperatures due to compression between  $T_s$  and  $T_a$ , heat conduction predominates, and the temperature of the mixture will drop to the static terminal value  $T_s$ . Only in terminal temperatures of compression above  $T_a$  will explosion result.

Todes treats this case in the same manner as the others and finds a relation among the terminal temperature of compression  $T_a$ , the container temperature  $T_0$ , and the pressure  $p$ . This, then, is equivalent to equation (17), or rather (34)

$$\ln \frac{p}{T_a} = \frac{1}{\nu} \frac{E}{RT_a} + \frac{1}{\nu} \ln (T_a - T_0) + \text{const} \quad (46)$$

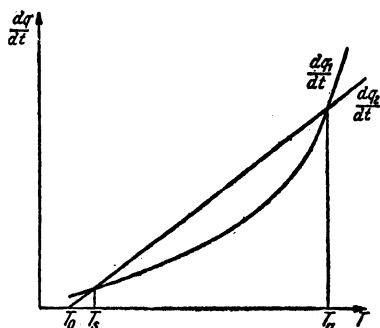


FIG. 10.—Ignition by adiabatic compression; heat production and conduction analogous to Figs. 1 and 2. (From Todes.)

To what extent the assumptions necessary for the derivation are fulfilled would have to be determined in each case. Analogous to the method in the preceding section, one can estimate an induction period  $\tau_i$  for the terminal temperature of compression  $T_a > T_s$ .

$$\tau_i \sim \frac{T_a^{\nu+1}}{p^{\nu-1} f(\gamma)} e^{E/RT_a} \quad (47)$$

The relation permits, under certain circumstances, the determination of the heat of activation of a reaction from observed periods of induction at various temperatures.

In all experiments with adiabatic compression, one must keep in mind that, besides temperature changes, a variation in the reaction velocities is caused by the rise in pressure at the same time.

These processes are important because a considerable number of so-called "ignition temperatures" are determined by adiabatic compression, and also because the condition of the unburned gas mixture in the combustion engine is described by the information given above. An improvement in the calculations might be possible by numerical integration.

**4. Examples of Thermal Explosions.**—Of the greater number of known reactions, only a few have been thus far identified as thermal explosions with any degree of certainty. Probably the examples of the decomposition of azomethane and ethyl azide already mentioned are such cases (cf. page 10). According to Sagulin,<sup>1</sup> the disintegration of chlorine monoxide,  $\text{Cl}_2\text{O}$ , should lead to a thermal explosion. As an

<sup>1</sup> SAGULIN, A.B., *Z. physik. Chem.*, Sec. B, 1, 275 (1928).

empirical relation for the critical pressure of explosion, he finds

$$\log \frac{p_k}{T_k} = \frac{A}{T_k} - B$$

with  $A = 2500$ . According to Hinshelwood,<sup>1</sup> the disintegration reaction of  $\text{Cl}_2\text{O}$  takes a homogeneous course according to the second order, corresponding to an expression of velocity

$$v = kp^2e^{-21,000/RT}$$

which would lead to  $A = 2300$ .

This cannot be reconciled with the much more complicated effect that this reaction shows according to Schumacher.<sup>2</sup>

Farkas<sup>3</sup> has studied more closely the reaction of hydrogen sulphide with oxygen and found that a chain reaction exists, to be sure, and that the condition of the wall has a strong influence on the velocity of reaction and the appearance of the explosion, but that a marked increase in temperature precedes the latter. This rise was determined by use of a Wollaston wire stretched in the container as a resistance thermometer. It was observed, for example, that, at 300 mm pressure and an initial temperature of 250°C, explosion took place after 14.8 sec. During this time, the temperature had increased to 342°C, which represents an extraordinary rise in the induction period.<sup>4</sup> According to Farkas, the critical limit of explosion can, to be sure, be represented by an exponential relation, but the heat of activation varies with the condition of the wall. This should not be the case in thermal explosion. Clearly one is dealing with a process here in which, in addition to chain-branching, the production of heat is essential for the appearance of explosion. It is remarkable that complete transformation is not always effected immediately in the explosion, but that a series of explosions, up to five, can follow upon one another.

Appin, Chariton, and Todes<sup>5</sup> have studied the thermal disintegration

<sup>1</sup> HINSHELWOOD, C.N., *J. Chem. Soc.*, 1923, p. 2730.

<sup>2</sup> Cf. the presentation by H.J. Schumacher, "Chemische Gasreaktionen," Dresden, 1938.

<sup>3</sup> FARKAS, L., *Z. Elektrochem.*, **37**, 670 (1931). Cf. also THOMPSON, H.W., *J. Phys. Chem.*, **35**, 3639 (1931). TAYLOR, H.A., and E.M. LIVINGSTON, *J. Phys. Chem.*, **35**, 2676 (1931); **36**, 1041 (1932). THOMPSON, H.W., and N. ST. KELLAND, *J. Chem. Soc.*, 1931, p. 1809. THOMPSON, H.W., *Nature*, **127**, 629 (1931). Cf. also SEMENOFF, N., "Chemical Kinetics and Chain Reactions," Oxford, 1935.

<sup>4</sup> In a thermal explosion, the rise should amount to about  $RT^2/E$ . Thus the rise above seems high. The suspicion therefore arises that a catalytic reaction takes place on the surface of the wire, as also in other cases [in ethanoxidation in the presence of methyl nitrite]; GIMMELMANN, G.A., and M.B. NEUMANN, *Acta Physicochim. URSS*, **7**, 221 (1937).

<sup>5</sup> APPIN, A., J. CHARITON, and O. TODES, *Acta Physicochim. URSS*, **5**, 654 (1936).

and the explosion of methyl nitrite. Between 210° and 240°C and at pressures of 5 to 15 mm Hg, the course of the disintegration is homogeneous and, according to the first order with a velocity constant,

$$k = 2.5 \cdot 10^{14} \exp \left( - \frac{39,500}{RT} \right)$$

At higher temperatures and pressures, the disintegration becomes explosive. For disintegration in a cylindrical glass container with an inner diameter of 3.4 cm and a volume of 130 cm<sup>3</sup>, the following pressure limits of explosion were found:

|                    |     |     |     |     |     |     |     |       |     |       |
|--------------------|-----|-----|-----|-----|-----|-----|-----|-------|-----|-------|
| Temp., °C.....     | 324 | 311 | 294 | 280 | 273 | 261 | 256 | 249.5 | 248 | 246.5 |
| $p_k$ , mm Hg..... | 4.2 | 5.5 | 8.5 | 13  | 17  | 34  | 46  | 87    | 107 | 163   |

The critical pressures of explosion, to be sure, decrease rapidly and regularly with rising temperature, but the dependence is nevertheless not to be represented by a simple relation between  $\log(p_k T_k^n)$  and  $1/T_k$ . According to the authors, this might be due to the fact that, at higher temperatures, the induction periods for ignition are either just about as long or shorter than the time that the gas needs for streaming into the reaction container. Thus the first part of the mixture might have reacted before the rest streamed in and the ignition as a whole would suffer. Whether this interpretation is correct would have to be tested in further experiments.

The same reaction has been studied in greater detail below 240° by Steacie and his associates (*cf.* Schumacher, "Chemische Gasreaktionen"). It takes its course by a chain pattern, which, however, need not exclude the possibility of thermal explosion.

From the observed dependence of the periods of induction on the temperature, an activation energy of about 35 kcal is computed, in sufficient conformity with the value found for the velocity of reaction. From all these observations, the authors feel confident that they can deduce the presence of a thermal explosion.

According to Gimmelman and Neumann<sup>1</sup> (*cf.* Chap. XI), ethane combustion in the presence of methyl nitrite is a process compounded of chain and thermal processes. Methane combustion, which according to Sachse can be considered a thermal explosion, is treated in Chap. XI.

The process of thermal explosion is probably more frequently realized in those cases in which, at higher pressures, auto-ignition takes place with a short induction period. On account of experimental difficulties, these processes have not been studied very much.

**5. Ignition by Heated Surfaces.**—Until now we have treated the process in which a considerable mass of gas was heated either by heating

<sup>1</sup> GIMMELMAN, G.A., and M.B. NEUMANN, *Acta Physicochim. URSS*, **7**, 221 (1937).

the container or by adiabatic compression. We shall now consider the case in which a considerable quantity of cold or moderately warm gas is brought into contact with a hot surface at only one point—a process that is less favorable to ignition than the one formerly discussed.

In ignition by heated surfaces (*e.g.*, red-hot wires), catalytic influences in general play a considerable role. According to whether the surface in question introduces or breaks off reaction chains especially vigorously, the surface will begin to be effective at particularly low or only at very high temperatures.

We shall here again disregard these influences completely and shall study the ignition insofar as it is explainable exclusively by thermal effects. We can, as we shall later (pages 45ff.) in the case of spark ignition, perform a rough calculation by comparison with the corresponding conditions in thermal explosion in a heated container. We shall

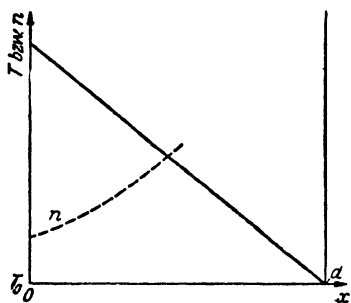


FIG. 11.—Variation of the temperature and concentration of the initial materials  $n$ , with reaction in a chamber heated on one side, with  $x = 0$ , of the length  $d$ ; qualitative.  $bzw = or$

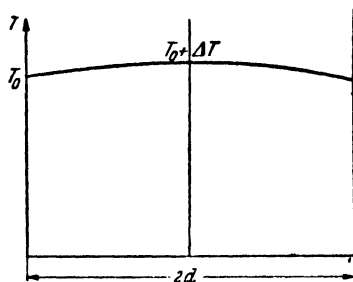


FIG. 12.—Variation of the temperature with reaction in a chamber heated on all sides of the length  $2d$ ; qualitative.

especially consider a cylindrical container of the length  $d$  (Fig. 11) whose left end surface is to be heated to the temperature  $T_1$ , while the right end is to be at room temperature  $T_0$ . A passage of heat through the cylinder casing is to be disregarded. Without reaction, we should have a linear drop in temperature in a static condition of  $T_1$  to  $T_0$  with a heat flow proportional,  $\sim (T_1 - T_0)/d$ . If, on the other hand, we had a reaction in a container heated on all sides with a distance from the wall of  $2d$  (Fig. 12), the maximum static temperature would be  $T_0 + \Delta T$ , existing before an explosion, only a few per cent higher than the wall temperature  $T_0$  (*cf.* page 17). The flow of heat to one side would be about  $\sim \Delta T/d$ , that is, only a few per cent of the flow appearing in the case of Fig. 11. If, therefore, the velocity of reaction in Fig. 11 is to increase without limit, then, because of the higher losses of heat, this velocity of reaction in the neighborhood of the hot wall will probably have to be ten to one hundred times higher than the temperature  $T_0 + \Delta T$  of Fig. 12. That

would mean, however, that the hot surface would have to be considerably warmer than the walls of a closed container if the same mixture is to be ignited. If, as is usually the case, the heat conduction conditions were less favorable than in Fig. 11 (a small igniting surface in a larger gas mass), one must raise the temperature correspondingly higher to compensate for the increased heat losses. At any rate, the theory of heat informs us that, under certain circumstances, hot surfaces can be brought into a gas mixture, the temperatures of which lie considerably above the previously determined "ignition temperatures," without causing general ignition.

As in the examples of induced ignition to be treated later, it is not difficult in ignition by hot surfaces to set up a differential equation, as long as it is kept on the basis of a pure theory of heat. If we restrict ourselves to the easily generalized linear problem of Fig. 11, we get for the temperature change with time

$$\frac{\partial T}{\partial t} = \kappa \frac{\partial^2 T}{\partial x^2} + n\rho \frac{Q}{c} \exp\left(-\frac{E}{RT}\right) \quad (48)$$

in which the first member to the right gives the cooling by conduction, the second the heating by chemical reaction.<sup>1</sup> For the sake of simplicity we have assumed a reaction of the first order and therefore included  $n$ , the momentary mol-number of the initial material contained in a unit volume as the factor.  $\rho$  therefore represents the coefficient of velocity. An integration of this equation offers the same difficulty as does the case of spark ignition (*cf.* Chaps. II and X) and could be solved numerically only in the individual case.

Just as in spark ignition, so here too an exact treatment would demand taking into account the influence of diffusion. In the proximity of the hot plate (Fig. 11), the reaction will be most vigorous. As a result, a drop in concentration will occur for the initial products (dotted line of Fig. 11), and a diffusion stream directed against the hot stream will constantly lead new initial material into the zone of the most vigorous reaction (and conversely, of course, the reaction products will constantly be led off out of this zone by diffusion). For the concentration, which changes by diffusion (diffusion coefficient  $D$ ) and chemical reaction, there

<sup>1</sup> In this equation  $\frac{\partial T}{\partial t} = \kappa \frac{\partial^2 T}{\partial x^2}$  would be the general heat-conduction equation for the one-dimensional case (*cf. e.g.*, FRANK-MISES, "Differential- und Integralgleichungen der Physik," F. Viewig & Son, Brunswick, 1930/35);  $\kappa$  means the "ability to conduct temperature,"  $\kappa = \frac{\lambda}{c\sigma}$ , if  $\lambda$  is the ability to conduct heat,  $c$  the mean specific heat per mass unit, and  $\sigma$  the density. For the sake of simplicity,  $\kappa$  is considered constant. The second member in (48) contains the raising of the temperature by chemical reaction. The corresponding relations are discussed in greater detail on p. 117.



would result an equation analogous to (48)

$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2} - n\rho \exp\left(-\frac{E}{RT}\right) \quad (49)$$

It would now be necessary to solve the system of simultaneous, partial differential equations (48) and (49). (Corresponding equations would have to be given for spark ignition; cf. Chap. II, page 49.)

We shall derive one more relation, effective for the quasistatic case, *i.e.*, as long as no explosion occurs and the entire change of concentration remains small.<sup>1</sup> Therefore

$$0 \cong \frac{\partial T}{\partial t} = \kappa \frac{\partial^2 T}{\partial x^2} + n\rho \frac{Q}{c} \exp\left(-\frac{E}{RT}\right) \quad (48a)$$

$$0 \cong \frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2} - n\rho \exp\left(-\frac{E}{RT}\right) \quad (49a)$$

From this it follows

$$\kappa \frac{\partial^2 T}{\partial x^2} = -n\rho \frac{Q}{c} \exp\left(-\frac{E}{RT}\right) = -\frac{Q}{c} D \frac{\partial^2 n}{\partial x^2} \quad (50)$$

$$\frac{\partial^2 T}{\partial x^2} = -\frac{QD}{\kappa c} \frac{\partial^2 n}{\partial x^2} \quad (50a)$$

or, with  $\zeta = \frac{QD}{\kappa c} n$

$$\frac{\partial^2 T}{\partial x^2} = -\frac{\partial^2 \zeta}{\partial x^2} \quad (51)$$

and integrated

$$T = -\zeta + \beta x + \gamma \quad (52)$$

The trend of the temperature and concentration appear about the same as in Fig.

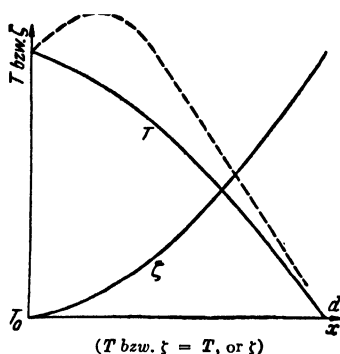


FIG. 13.—Variation of temperature and reduced concentration  $\zeta$  in a quasistationary condition; conditions as in Fig. 11, with the special expression of the text.

Something more that is important. The introduction of a heated surface need

<sup>1</sup> Strictly, a static condition can be achieved only if in  $x = d$  the reaction products are constantly conducted off through a semipermeable wall, and at the same time the used-up fresh gas is replaced.

13, in case we assume  $x = d$ ,  $T = T_0$ , and  $x = 0$ ,  $n = 0$ . The curvature of the graphs must be as in Fig. 13,  $\partial^2 T / \partial x^2$  must be negative, and  $\partial^2 n / \partial x^2$  must be positive. Basically, the latter need not hold for the whole range. We therefore assume that, at the right end of the graph, the substance used up by the reaction is constantly being supplied through a semipermeable wall, and that correspondingly the products of reaction are led off.

It appears that a distribution of temperature according to the dotted line in Fig. 13 can no longer belong to a quasistatic condition, because no logical curve of concentration for it is possible. Naturally, this is true only for the approximation we have been employing in all the material in this section.

Qualitatively, Fig. 13 shows some-

not necessarily lead to ignition, partly because, precisely in the hottest zone, the concentration of the initial material is reduced in strength and thus the velocity of reaction remains limited.

In this connection, an observation of Davy's should be discussed, *i.e.*, firedamp cannot be ignited by flameless-burning charcoal. Let us imagine the left wall in Fig. 13 to consist of burning charcoal of the temperature  $T$ . The difference here from the former case is that this wall is a source not only of heat but also of carbonic acid (and perhaps of carbon monoxide) as well as a reservoir for oxygen. We should therefore have to set up diffusion equations for these materials as well as for the reacting methane. But, even without them, it can be seen that in the proximity of the "wall" the excess of carbon monoxide (high capacity for heat effect of dilution) and the lack of oxygen must influence the combustion unfavorably, as experience shows.

For a quantitative treatment of this problem, it would probably be well to take into account diffusion (and probable conduction of heat) in only one layer bordering on the wall, as one usually does in dissolving processes, but otherwise to assume complete mixture.

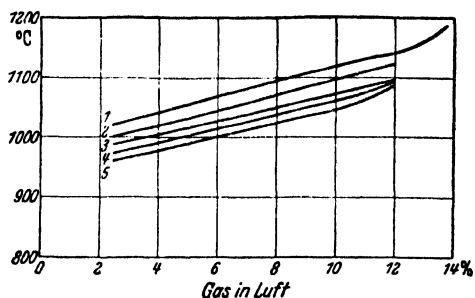
The most essential qualitative conclusion from the preceding is, generally speaking, substantiated by experience—that a heated surface introduced into a gas mixture, if it is intended to ignite it, must have a higher temperature than a container surrounding the gas would need to have, if auto-ignition is to result. Moreover, the smaller the heated surface of the hot body brought in contact with the gas, the higher the temperature must be. If (*cf.* page 45) the ignition temperatures determined for methane-air mixtures under the usual conditions lie in the neighborhood of about  $700^{\circ}\text{C}$ , nickel rods of a few millimeters to a few centimeters in diameter must be heated to at least about  $1000^{\circ}\text{C}$  if they are to be brought into contact with a large mixture of methane and air and are to ignite it.

In the ignition of gas mixtures by means of metal rods and wires, a number of surprising facts are revealed. It will therefore be necessary to consider these at this point. First of all, it has been noted<sup>1</sup>—and this is not surprising—that the thinner the igniting strip of metal, the hotter it must be, as can be seen from Fig. 14 (taken from Coward and Guest).

The comparison between the various metals is very striking, however. If we consider platinum, which is catalytically very active and greatly hastens the reaction on its surface, we do not find ignition at especially low temperatures; on the contrary, the metal must be heated considerably, and most of all with more active gas-air mixtures of medium composition, to about  $350^{\circ}$  higher than corresponding nickel strips (*cf.* Fig. 15).

<sup>1</sup> COWARD, H.F., and P.G. GUEST, *J. Am. Chem. Soc.*, **49**, 2479 (1927).

First of all it should be pointed out—and Coward and Guest have already noted this—that this finding does not contradict the well-known fact that an oxygen-hydrogen mixture  $H_2-O$  can be ignited by platinum



(Gas in Luft = gas in air)

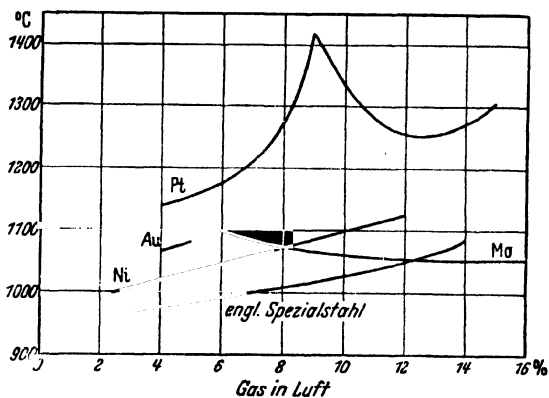
FIG. 14.—Ignition of natural gas and air mixtures by nickel rods (composition of the natural gas: 93.2 per cent  $CH_4$ , 3.3 per cent  $C_2H_6$ , 1.5 per cent  $C_3H_8$ , 0.5 per cent  $C_4H_{10}$  etc.; 1.5 per cent  $N_2$ ).

Curve 1  
2  
3  
4  
5

Breadth of the metal strip, inches

$\frac{1}{4}$   
 $\frac{1}{2}$   
 $\frac{3}{4}$   
1  
 $1\frac{1}{2}$

Thickness of the strip 0.102 cm, length 4.25 inches. (From Coward and Guest.<sup>1</sup>)



(Gas in Luft = gas in air  
(engl. Spezialstahl = English special steel))

FIG. 15.—Ignition of natural gas and air mixtures by various metallic surfaces. (From Coward and Guest, p. 26.)

asbestos, platinum sponge, or very thin platinum wire. In this case, mass and heat capacity of the solid are so small that it can be heated to red or white heat as a result of the catalytic transformation before ignition takes place.

<sup>1</sup> COWARD, H.F., and P.G. GUEST, *J. Amer. Chem. Soc.*, vol. 49, p. 2479 (1927).

In metal strips, the heat capacity is very great, and they therefore not only do not heat very much, but by means of heat conduction they even hinder the gas in their proximity from becoming noticeably hotter than the metal. Only by taking into account the great heat capacity of the metal does the unfavorable ignition effect of catalytically active metals become understandable. As we have seen above (Fig. 13), a drop in concentration and temperature will occur as long as the ignition point has not been reached. This drop is of such a nature that the fresh gas at the surface of the metal is more or less completely used up and the products of reaction are constantly diffused from this surface while new fresh gas is diffused toward it. Without heat conduction from the reacting (hotter) gas to the metal, the following explanation of the phenomenon by Mason and Wheeler<sup>1</sup>—in itself correct—would not be intelligible. "The mixture that immediately surrounds the heated surface can be used up so fast that it is not capable of propagating a flame, while the reaction takes place only at or near the heated surface, even if the temperature there rises far above the true ignition temperature of the gas."

If one imagines, for instance, that the volume of the piece of metal is replaced by one equal to the explosive gas mixture, which is heated to the same temperature as the metal ordinarily is, then raising the ability for reaction at the boundary of this volume could only aid the ignitibility. The same would be true of a transition from a catalytically less active to a highly active metal, as long as the heat absorption of the metal is ignored. Qualitatively, approximately the following would result in the proximity of a heated piece of platinum and a piece of nickel heated to the same temperature. We plot the concentration of the fresh gas and the temperature as a function of the distance from the metal surface. In the case of nickel, let this distribution be given by Fig. 16. The concentrations of the component parts of the fresh gas drop toward the metal (those of the reaction products take an opposite course). The temperature drops on the outside at a greater distance from the metal surface. At a certain distance  $d$  from the surface, the temperature could also pass through a maximum. If the loss of heat by conduction is small under these conditions (a slight bend of the temperature curve at the maximum), the temperature can rise constantly under certain circumstances and ignition can result. Conversely, the velocity of reaction at the point of the maximum temperature is high (not too low a concentration of fresh gas at this point).

In the case of platinum, one would have to imagine the corresponding curves perhaps in the following manner (Fig. 17). In the immediate

<sup>1</sup> MASON, W., and R.V. WHEELER, *J. Chem. Soc.*, **121**, 2079 (1922); **125**, 1869 (1924).

proximity of the platinum surface, there is a very active reaction. Since the reaction is not confined strictly to the surface, there is, in the immediate proximity, a rise in temperature in the gas with a relatively steep maximum (which, however, under certain circumstances is absolutely lower than nickel), with a sharp bend in the temperature curve and thus a great loss of heat at the maximum, especially toward the side of the greater drop in temperature, *i.e.*, toward the metal surface. The conduction of heat can therefore balance out the production of heat by chemical reaction (caused probably by the speed with which the fresh gas can be supplied by diffusion), and hence no ignition takes place. Coward and Guest have also shown that thorough turbulence of the gas causes ignition at a lower temperature of the metal, obviously

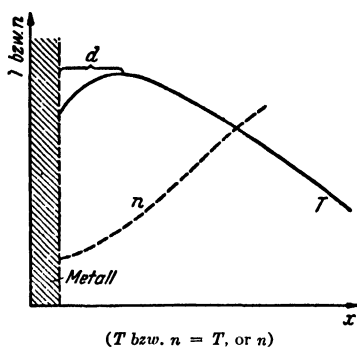


FIG. 16.

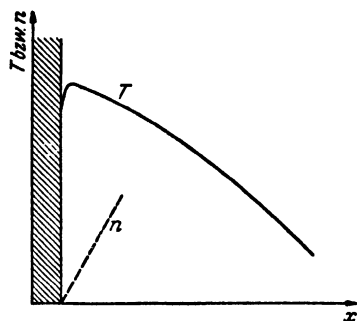


FIG. 17.

FIGS. 16 AND 17.—Variation of temperature and concentration in the proximity of a metal that is catalytically slightly active (left) or highly active (right).

because fresh gas is led to the metal more rapidly, and thus the chemical change is accelerated, although the loss of heat is of course greater too.

For a quantitative treatment of these phenomena of ignition on hot surfaces, the differential equations above should suffice. Here too, however, an adequate knowledge of all magnitudes of reaction velocity would be necessary for integration, and this integration would have to be carried out numerically.

Coward and Guest have also determined experimentally how much gas is burned before ignition by contact with platinum and nickel. The products of combustion, measured by  $\text{CO}_2$  that had been formed, were about twenty times greater in platinum than in nickel under the same conditions. If, in spite of this fact, the gas does not reach ignition temperature in the case of platinum, the cause might be that the conversion takes place so much closer to the platinum surface that the temperature drop toward it and the loss of heat to it are so much greater that the gas temperature is nevertheless maintained lower.

Such experiments make clear why it is possible to keep an Otto

engine going under extreme conditions in which the exhaust becomes red-hot. Only because the conditions for ignition are so unfavorable on a hot surface can such an engine work at all without premature ignition.

Silver<sup>1</sup> investigated the ignition of explosive mixtures by hot spheres "shot in." A platinum sphere of 4 mm diameter, which was heated to 1200°C, was unable to ignite a 10 per cent methane-air mixture. Systematic experiments with more readily ignitable illuminating gas and air mixtures were therefore made, and it was especially tested whether the temperature of the spheres used had not appreciably dropped on the way from the oven into the explosive mixture. It was observed that the ignition temperatures were rather high—for 10 per cent illuminating gas in air, between 855° and 1140°—and that the ignition temperatures were higher as the spheres became smaller. The two limiting values given correspond to sphere diameters of 0.50 and 0.11 cm. The duration of heating of the gas mixture in the neighborhood of the sphere is indicated by the fact that the spheres were shot in with a velocity of about 4 m/sec.

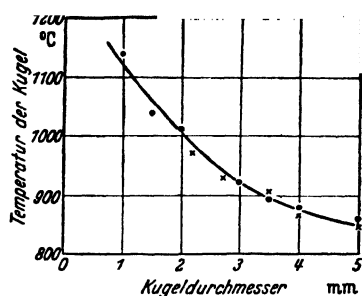
Under the experimental conditions that prevailed, the material of the spheres clearly has only a small effect, since experiments with quartz spheres gave almost the same ignition temperatures as those with platinum spheres (Fig. 18). The rapidly propelled sphere exerts its effect on the gas it passes through apparently only by heat transfer, and the chemical reaction takes place to a noticeable extent only after the passing of the sphere.

Because of the high ignition temperatures, no measurements for methane could be carried out. The only result obtained was that apparently an 8 per cent methane and air mixture was ignited at about 1200°C by a platinum sphere of 6.5 mm diameter.

On the other hand, measurements could be carried out on the more easily ignitable pentane. The following ignition temperatures resulted:

MIXTURE OF 3 PER CENT PENTANE IN AIR WITH PLATINUM SPHERES (FROM SILVER)

|                          |       |       |       |       |       |       |
|--------------------------|-------|-------|-------|-------|-------|-------|
| Sphere diameter, cm..... | 0.109 | 0.197 | 0.303 | 0.398 | 0.500 | 0.550 |
| Ignition temp., °C.....  | 1370  | 1240  | 1155  | 1065  | 1040  | 1005  |



(Temperatur der Kugel = temperature of the sphere  
Kugeldurchmesser = diameter of the sphere)

FIG. 18.—Ignition of a 10 per cent illuminating gas and air mixture by introducing hot spheres; the dots represent platinum spheres and the crosses represent quartz spheres. The lowest temperature necessary for ignition depends on the diameter of the sphere. (From Silver.)

<sup>1</sup> SILVER, R.S., *Phil. Mag.*, (7), 23, 633 (1937).

The same ignition temperatures were obtained by using quartz spheres and also with hydrogen, but not quite so well.

It is striking that the ignition temperatures found for hydrogen and air mixtures are lower than for pentane; whereas, by most of the other methods, pentane yields much lower ignition temperatures. The following were measured:

MIXTURE OF 20 PER CENT WATER VAPOR IN AIR WITH PLATINUM SPHERES (FROM SILVER)

|                          |       |       |       |       |       |
|--------------------------|-------|-------|-------|-------|-------|
| Sphere diameter, cm..... | 0.197 | 0.240 | 0.303 | 0.500 | 0.500 |
| Ignition temp., °C.....  | 930   | 880   | 840   | 810   | 795   |

Silver tries a much simplified theoretical treatment of the results. He is of course aware of its limited applicability. It is essentially an adaption of Semenov's theory of heat. He proceeds from the ignition equation (which we have derived formerly)

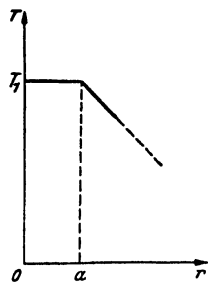


FIG. 19. Variation of the temperature in the proximity of a heated sphere. (From Silver, p. 29.)

$$\frac{\partial T}{\partial t} = k \left( \frac{\partial^2 T}{\partial r^2} + \frac{2}{r} \frac{\partial T}{\partial r} \right) + \alpha e^{-B/T}$$

in which the first terms on the right side give the cooling by conduction in the sphere for the symmetrical case, and the last gives heating by heat of reaction. Since a direct integration is not possible, Silver tries the following approximation, which follows Semenov's ideas but is even less exact. He makes the following assumptions: The layer of gas in the immediate proximity of the surface is momentarily heated to the temperature  $T_1$ . The loss of heat to the outside (outside temperature  $T_0$ ) per unit of surface is given equal to  $A(T_1 - T_0)$ ; this gradient is assumed to be constant within the thin heated layer at the surface (Fig. 19). The loss of heat of a layer

adjacent to the surface of the sphere with a thickness of  $dr$  is found ( $a$  is the radius of the sphere) as

$$\sim 8\pi a A (T_1 - T_0) dr$$

The heat production in this layer is

$$\sim 4\pi a^2 dr \alpha e^{-B/T_1}$$

Equating both expressions should give the condition for ignition

$$8\pi a A (T_1 - T_0) dr = 4\pi a^2 dr \alpha e^{-B/T_1}$$

or

$$a = \frac{2A}{\alpha} (T_1 - T_0) e^{+B/T_1}$$

Silver tests this condition by plotting  $\log \frac{T_1 - T_0}{a}$  against  $\frac{1}{T_1}$  and finds it verified quite well in the three cases studied by him (Fig. 20). The "activation energies" ( $BR$ ) lie close together for all three cases studied. He finds

## "ACTIVATION ENERGY" (FROM SILVER)

|                                 |            |
|---------------------------------|------------|
| Pentane oxidation.....          | 20,520 cal |
| Illuminating-gas oxidation..... | 21,150 cal |
| Hydrogen oxidation.....         | 22,560 cal |

Note that a rectilinear relation between  $\log 1/a$  and  $1/T_1$  must be approximately obtained for every ignition law in which any power of  $a$  and an exponential function of  $1/T$  occur. Landau<sup>1</sup> also obtains such a relation

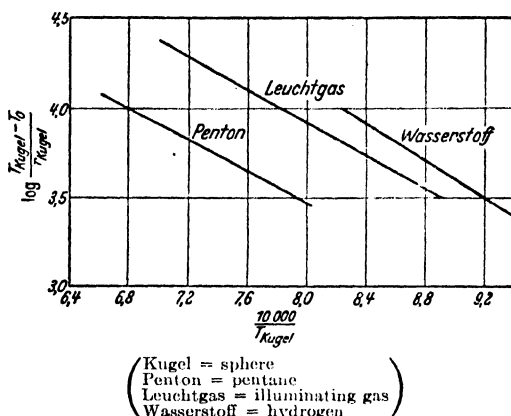


FIG. 20.—Experimental test of the relation derived by Silver; see the text. (From Silver, p. 29.)

(with a higher power for  $a$ ; Chap. XI) and finds that it is substantiated by Silver's findings, although serious objections to Landau's treatment must be raised from the standpoint of explosions by chain-branching.

In a more rational application of the theory of heat to this process, one might expect, as in similar cases, the conduction of heat as the function of a parameter  $a^2 kt$  and therefore rather  $a^2$  instead of  $a$  in Silver's relation. The result would be that the heat of activation found by Silver would have to be doubled, and this would agree better with the observed orders of magnitude.

It should be emphasized at this point (just as in the case of spark ignition; cf. Chap. II) that the necessary taking into account of diffusion phenomena must not necessarily destroy the form of the relations established, for the laws of diffusion are formally the same as those for heat conduction.

If the hot sphere is at rest and the air is streaming past it (Fig. 21), the temperature of the heated gas immediately behind the sphere reaches its maximum. We may assume approximately that a stream of gas of

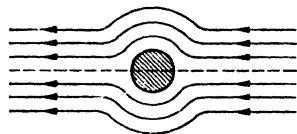


FIG. 21.

<sup>1</sup> LANDAU, *Chem. Rev.*, **21**, 245 (1937).



cylindrical form leaves the sphere, the diameter of which is about proportional to the diameter of the sphere (this would mean that the heated mass of gas is proportional to the square of the diameter of the sphere, to which also the heat-conducting surface of the sphere is proportional). Thus we have a uniform, radial symmetrical problem of heat conduction, and the conditions would be similar to those upon which we base the simplified theory of heat of spark ignition. To be sure, convection and turbulent flow are added as disturbing factors, but qualitatively little would be changed.

### SUPPLEMENT

#### GENERAL DISCUSSION OF EXPERIMENTAL DATA ON IGNITION TEMPERATURES<sup>1</sup>

As has been shown above in a general way, the appearance of ignition in an explosive mixture depends not only on the temperature to which the mixture has been heated, but also on a series of other factors dependent on the one hand on the chemical processes that take place in the mixture, and on the other hand on constants in the apparatus and the physical properties of the gas mixture (*e.g.*, heat conductivity, specific heat). It is therefore clear that there can be no definitely determinable constant temperature of ignition for a given substance, which could be so defined that above this critical temperature the explosive mixture would ignite, but below it would react not at all, or only slowly. As can be seen from the available experimental material on temperatures of ignition, these temperatures, determined by various methods, show considerable variations even for the same mixtures; and, even when the same methods are employed, the point of ignition must be dependent on the measurements and the material of the apparatus used. The criterion for the appearance of a heat explosion is, after all, this, that by means of chemical reaction more heat is always liberated than can be conducted off. The speed with which the heating of the gases takes place above the initial temperature (the difference of heat release and heat loss) decreases initially to a minimal value as the result of the shape of the curves for heat production and heat loss. If, after reaching this point, it again increases, the reaction goes over into explosion; and the time elapsing until this minimum is reached is called the "induction period." During this induction period, which can naturally be very short, a definite portion of the mixture capable of reaction must be converted, for only by means of the reaction heat thus generated is explosion possible. With decreasing initial temperature, and with constant conditions prevailing otherwise, the time until the minimum of the velocity of heating has elapsed increases and can, under certain circumstances, be relatively long (order of magnitude 10 sec). From this it is evident that, conversely, disregarding other influences, higher ignition temperatures must be obtained when the induction period is decreased. If, for example, in order to determine the ignition temperature of a mixture, the mixture is allowed to flow over an oven heated to a specific temperature, it will (depending on the velocity of the stream) remain at its maximum temperature for varying lengths of time; and ignition takes place if this time is longer than the induction period at this temperature. Otherwise ignition could take place only at a higher oven temperature, during a shorter induction period, at most equal to the period of contact. From the outset, therefore, it cannot be expected, for example, that one can arrive at the same values of ignition temperatures by this method as when one puts the mixture into a closed

<sup>1</sup> By L. v. Müffling.

container and leaves it to itself for an indeterminable length of time. The most important experimental methods by which ignition temperatures have been found are summarized here.

1. The explosive mixture flows through a combustion tube of known maximum temperature.

2. The mixture is introduced into a container of known temperature.

3. The mixture is compressed adiabatically, and the temperature is computed from the relation between the initial and final volumes or pressure.

4. The individual gases are heated separately in concentric tubes and mixed at a known temperature.

- 4a. The gases are heated individually until just before the maximum temperature, are mixed very quickly, and the mixture is then brought immediately to the maximum temperature.

5. A drop of a liquid fuel, or a stream of combustible gas, is introduced into a space of known temperature containing air or oxygen.

- 5a. A stream of combustible gas and a stream of air or oxygen are individually heated to a known temperature and then impinged upon each other.

6. The mixture is brought to ignition in a soap bubble by means of a platinum wire of known temperature.

7. The mixture is ignited by the shooting in of bodies heated to a known temperature.

8. The mixture is heated by inserting metal rods heated to a known temperature.

Regarding method 1, it should be noted that there is no uniformly defined temperature of the mixture. The mixture will heat itself within a definite time from the outside temperature to the maximum temperature. Reaction sets in even before the maximum temperature is reached, however, and the mixture will have a different composition when reaching the maximum temperature than at the beginning. On the other hand, one cannot find out how long the mixture remains at the maximum temperature and whether the latter exactly coincides with the oven temperature measured. These last two circumstances become especially dubious if high velocities of flow are applied to avoid a considerable pre-reaction.

In the second method, these difficulties connected with flow velocities do not occur. Naturally the mixture must first heat itself from the outside temperature to the temperature of the container, and reaction takes place; but then the mixture is, for an arbitrary length of time, at a uniformly defined temperature, and ignition is observed even when the induction period is relatively long. It can be assumed that, by means of this method, a minimum value for the ignition temperature of the gas in question can be obtained under the conditions chosen (pressure, etc.). Of course, these values are also to be considered only relatively, for the apparatus (size, shape, and material of the reaction vessel) is always the determining factor when the heat of reaction is computed (disregarding for the moment the special wall influences in chain reactions) and is thus of considerable influence on the ignition temperature. For example, higher ignition temperatures are noted for narrow containers than for wide ones, no matter with which reaction one may be dealing. At any rate, if a comparison of the various values received by various authors is to be made possible, an exact list of the details of apparatus is necessary.

The third of the methods given above has the advantage that a mixture of known composition is heated evenly in a very short time to the final temperature (naturally one takes into account conduction adjacent to the cold walls) and a pre-reaction is practically excluded. Compared with the preceding method, the difference is that the container walls remain at practically the initial temperature before compression, and there is in comparison a very great conduction of heat, thus making the dimen-

sions of the container a considerable factor. The speed of heat production must therefore be greater from the very outset than in method 2, *i.e.*, the observed ignition temperatures must be higher than those observed in method 2. To be sure, a direct comparison with the values of method 2 is not possible because the mixture in general has an essentially higher pressure. Thus, in the first place, the reaction is usually hastened; and, in the second place, the quantity of heat produced per unit of volume is correspondingly increased. By means of these two effects, the influence of the greater conduction of heat can, according to the conditions of experiment, be compensated for to a certain extent, or overcompensated for. The method has the disadvantage that one cannot measure the final temperature of compression but must compute it from the compression relations or from the compression pressure. But of course the nonadiabatic action of the gases during compression makes correction necessary and difficult to determine, and thus the determination of the temperature can be only approximately correct.

In method 4, it should be noted that pre-reaction at an unknown temperature is excluded. To be sure, ignition in this case is considerably dependent on the mixing process. Starting with the two pure substances to be mixed, all mixing conditions are present contemporaneously in the reaction space, and ignition will take place at the point of mixture composition most favorable to it. To be sure, the values are found to be in good agreement, but reaction-kinetic conclusions, for example, are hardly possible on account of the undefined mixture composition.

Method 4a is a compromise between methods 1 and 4. If one wants to achieve as complete a fusion as possible in order to get as unified a mixture as possible, pre-reaction at the mixing temperature and in continued heating to the maximum temperature cannot be excluded, especially since the reaction takes place with great velocity in proximity to the ignition point. If one raises the velocity of flow in order to minimize the pre-reaction, then the mixing is adversely affected, not to speak of the other effects discussed in flow experiments under method 1 above.

For method 5, the same considerations hold as for method 4. In the use of liquid fuels, vaporization must be considered, which also disturbs the constancy of temperature.

All the methods discussed hitherto had the common characteristic that in applying them the entire mixture is heated to the critical temperature. In the following methods, on the contrary, only a small part of the gas mass will be brought to the desired temperature, or to ignition, as the case may be, while the remaining part remains cold. After ignition at the hot point, the reaction spreads in the form of a flame through the mixture. For this form of ignition, not only is the temperature of the igniting body (let us say, as in method 6, a platinum wire) critical, but also the entire mass of energy conducted to it (*e.g.*, in method 7, experiments by Silver on the influence of the size of the heated body on the ignition temperature; *cf.* page 30). By the introduction of a hot body at one place in the gas mass, a strong convection stream forms, which leads the heated portions of the mixture away from the hot place and leads cold portions to it. The individual gas portions will therefore take on only for a very short time (if at all, precisely) the temperature of the heated body, and they must during this time go through the induction period, if ignition is to result. One can therefore assume that the ignition temperatures thus established are considerably higher than those arrived at by the methods above described. These considerations are valid in a very general way for the last three of the methods mentioned. As a detail, it should be mentioned that, in using metals (*e.g.*, platinum, which can have a possible catalytic effect on the reaction), the ignition temperature, in contrast to noncatalytic bodies, can be considerably changed [*cf.*, for example, Coward and

Guest (16)<sup>1</sup>. In experiments according to method 7, in which a spherical body of metal or quartz is shot through the mixture, one must consider a particularly short induction period. The ignition temperatures determined according to this method are correspondingly high. How great the influence of the total energy is can be seen in the dependence of the temperature of ignition on the size of the spheres. In addition, it must be taken into account when applying this method that the temperature of the sphere when entering the gas mixture cannot be measured directly but can be arrived at only approximately. Also, in the case of ignition by means of a hot metal wire, temperature measurement is possible only with relatively wide limits of error.

In order to show how far the ignition temperatures found by various methods and under changing conditions of experiment can vary, we give the findings of various authors for hydrogen and air mixtures (Table 1).

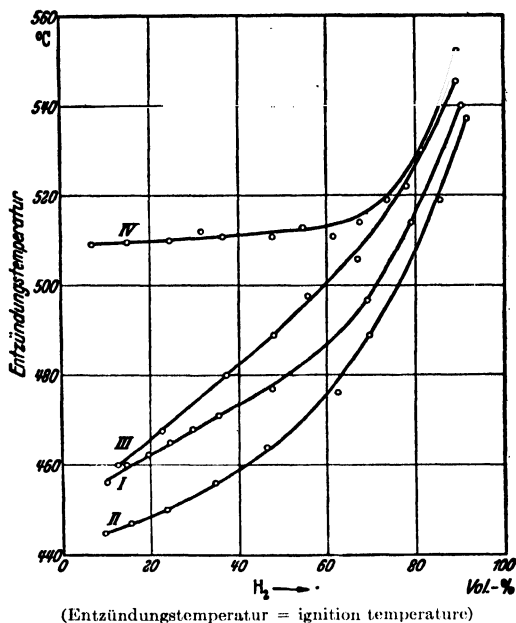
TABLE 1

| Method | Author                       | Composition of mixture, % H <sub>2</sub> | Ignition temperature, °C | Other data                                      |
|--------|------------------------------|--|--------------------------|---|
| 1      | Emich (1)                    | 28.5                                     | 609                      |   |
| 2      | Mallard and Le Chatelier (2) | 28.5                                     | 550                      |   |
| 2      | Taffanel and Le Floch (3)    | 28.5                                     | 590                      | Container with 350 cm <sup>3</sup> volume       |
| 2      | Taffanel and Le Floch (3)    | 28.5                                     | 625                      | Container with 9 cm <sup>3</sup> volume         |
| 2      | Prettre (4)                  | 29.7                                     | 467                      | Containers of 24 and 100 cm <sup>3</sup> volume |
| 3      | Dixon and Crofts (5)         | 28.5                                     | 571                      |   |
| 3      | Tizard (6)                   | —  | 410                      |   |
| 4      | Holm (7)                     | —  | 470                      |   |
| 4      | Dixon (17)                   | —  | 630                      | 0.5 sec induction period                        |
| 4      | Dixon (17)                   | —  | 572                      | 15 sec induction period                         |
| 4a     | Bloch (8)                    | 30                                       | 608                      | Dry mixture                                     |
| 4a     | Bloch (8)                    | 30                                       | 613                      | Moist mixture                                   |
| 5      | Moore (9)                    | —  | —                        |   |
| 5a     | Goldmann (10)                | —  | 580-590                  |   |
| 6      | McDavid (11)                 | 29                                       | 700                      |   |
| 6      | Withe and Price (12)         | 27                                       | 715-860                  |   |
| 7      | Silver (13)                  | 20                                       | 930                      | Diameter of the sphere, 0.2 cm                  |
|        |                              |  | 800                      | Diameter of the sphere, 0.5 cm                  |
| 8      | Coward and Wheeler (15)      | —  | —                        |   |

As can be seen, the maximum variation is over 500°, which justifies the assertion that the conditions of experiment are of decisive importance.

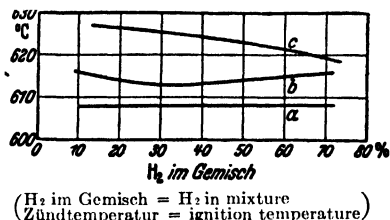
<sup>1</sup> In this supplement, numbers in parentheses refer to the references on p. 46.

On the variation of ignition temperature with the change of hydrogen concentration, there are reliable results by Prettre (*cf.* Fig. 22, curve I), according to method 2, and Bloch (*cf.* Fig. 23), according to method 4a. As can be seen, even the form of these curves depends on the method of experiment.



(Entzündungstemperatur = ignition temperature)

FIG. 22.—Ignition temperatures of  $H_2$ . Curve I,  $H_2$  in air. Curve II,  $H_2$  in  $O_2 + N_2$  mixture ( $O_2:N_2 = 1:1$ ). Curve III,  $H_2$  in  $O_2 + Ar$  mixture ( $O_2:Ar = 0.21:0.79$ ). Curve IV,  $H_2$  in  $O_2 + CO_2$  mixture ( $O_2:CO_2 = 0.21:0.79$ ). (From Prettre.)



( $H_2$  im Gemisch =  $H_2$  in mixture  
Zündtemperatur = ignition temperature)

FIG. 23.—Ignition temperatures of  $H_2$ . a,  $H_2$  in air (dry). b,  $H_2$  in air (moist, 2.3 per cent  $H_2O$  content). c,  $H_2$  in  $O_2 + CO_2$  mixture ( $O_2:CO_2 = 0.21:0.79$ ). [From Bloch (8).]

Dixon finds, according to method 4, marked periods of induction for the ignition of  $H_2$ -air mixtures which change with the temperature (*cf.* Fig. 24). In this method, one can assume with certainty, however, that the delay in ignition is principally due not to the chemical reaction but to processes of mixing. Other authors in very careful experiments according to other methods, especially Prettre (4), have been unable to find significant induction periods precisely in the case of  $H_2$  mixtures.

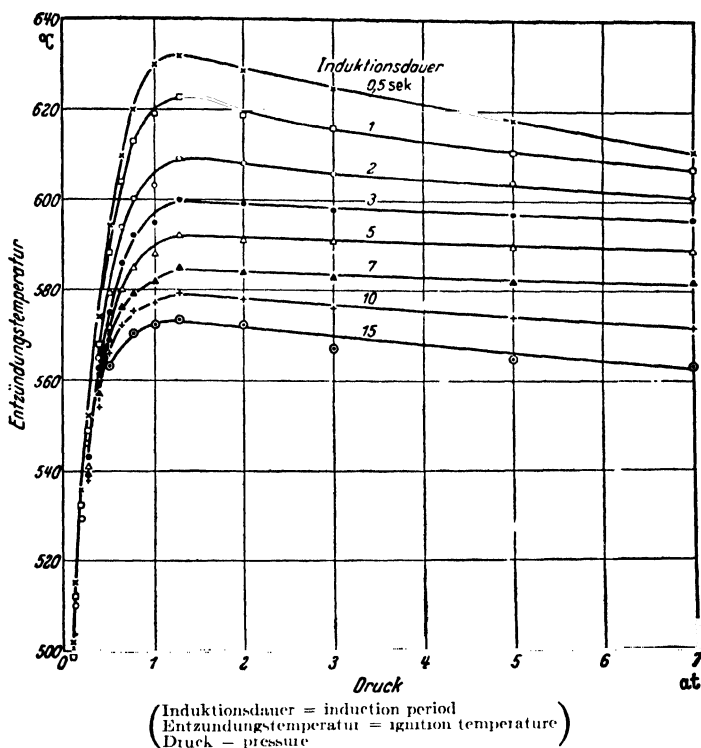


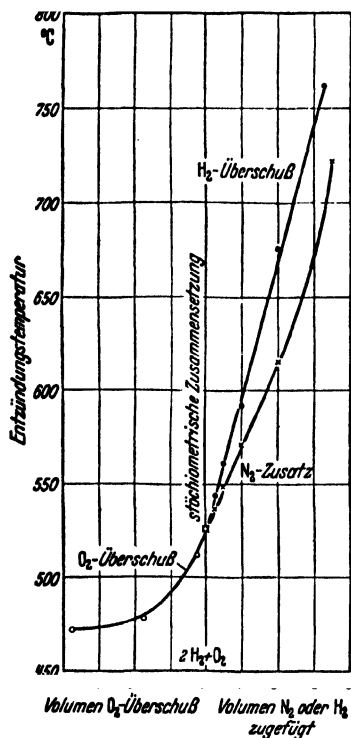
Fig. 24.—Ignition temperatures in  $H_2$  in dry air at various pressures. [From Coward (17).]

If hydrogen instead of air is mixed with pure  $O_2$ , the temperature of ignition changes relatively little, other experimental conditions remaining equal. For example, the following authors found

|  |           |  |
|--|-----------|--|
| Mallard and Le Chatelier (2) . . . . . | Method 2  | 70% $H_2$ 555°   |
| Falk (18) . . . . .                    | Method 3  | 70% $H_2$ 550°   |
| Dixon and Crofts (5) . . . . .         | Method 3  | 70% $H_2$ 533°   |
| Cassel (19) . . . . .                  | Method 3  | 70% $H_2$ 522°   |
| Dixon (17) . . . . .                   | Method 4  | $\left\{ \begin{array}{l} 625^\circ \text{ 0.5 sec ignition delay} \\ 575^\circ \text{ 10 sec ignition delay} \end{array} \right.$ |
| Goldmann (10) . . . . .                | Method 5a |  |
|  |           | 580–590°   |

Detailed studies on the influence of the composition of the mixture on the ignition temperature have been made by Dixon and Crofts (5) according to method 3 (adiabatic compression). Their results show that, with decreasing  $H_2$  concentration, the ignition temperature sinks till finally the lower limit of explosion under the conditions of the experiment has been passed. The experimental results of Dixon and Crofts can be seen from Fig. 25. Respecting the data of Falk, it should be pointed out that they must be too high because Falk allowed the piston in his compression cylinder to fall unhindered and the piston together with the weight used to accelerate it were thrown back. The ignition temperature was then taken from the compression

ratio at the lowest point of the piston. However, the experiments of Dixon, Bradshaw, and Campbell (20) and later especially those of Tizard and Pye (21) have already demonstrated that, even in adiabatic compression, ignition at the critical



Entzündungstemperatur = ignition temperature  
 Überschuss = excess  
 stöchiometrische Zusammensetzung = stoichiometric composition  
 Zusatz = addition  
 Volumen = volume  
 oder = or  
 zugefügt = added

FIG. 25.—Ignition temperatures of  $\text{H}_2\text{-O}_2$  mixtures of various compositions and with  $\text{N}_2$  additions. (Volumes of the additions equal many times the  $\text{O}_2$  quantity present in the stoichiometric mixture.) [From Dixon and Crofts (5).]

according to method 4, finds no marked change in the ignition temperature when changing from  $\text{H}_2\text{-O}_2$  to  $\text{H}_2\text{-air}$  mixtures.

temperature by no means takes place all at once. To be sure, the induction periods in the example under consideration are quite small (a few hundredths of a second), but they are nevertheless large enough so that, especially at a high piston velocity, the continuing compression raises the temperature by several hundred degrees above the minimum temperature necessary for ignition without causing a flame (20) or rise in pressure (21).

Dixon (17) also investigated, by method 4, the induction periods and the influence of pressure on the ignition temperature of  $\text{H}_2\text{-O}_2$  mixtures. It has already been mentioned above that the induction periods found according to this method need not necessarily coincide with the chemical processes. Concerning the dependence of the ignition temperature on pressure, the experiments showed that the ignition temperatures decreased with decreasing pressure, until, below 75 mm Hg, no ignition took place. The experiments extended from atmospheric pressure with an induction period of 0.5 sec (which Dixon selected as standard).

The differences found here between the ignition temperatures of  $\text{H}_2$  in  $\text{O}_2$  and air are negligibly small. Deductions on the course of reaction based on these measurements cannot be made because the composition of the mixture is known at no point. By other methods, somewhat greater differences were found in the ignition temperatures of  $\text{H}_2\text{-O}_2$  mixtures as well as in  $\text{H}_2\text{-air}$  mixtures.<sup>1</sup>

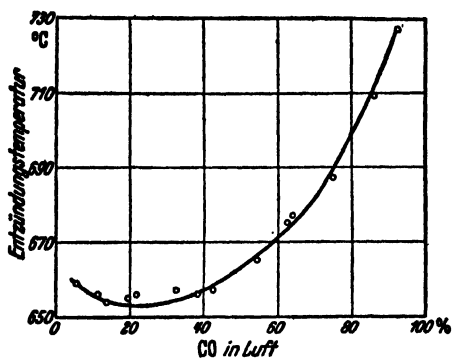
A series of studies have been made regarding the influence upon ignition temperatures of  $\text{H}_2\text{-O}_2$  mixtures diluted with inert gases like  $\text{N}_2$ ,  $\text{CO}_2$ , and Ar. The addition of  $\text{N}_2$ , depending on the method of experiment, either leaves the values pretty much unchanged or increases them slightly. Dixon (17), for example,

<sup>1</sup> For further data on the ignition temperatures of  $\text{H}_2\text{O}_2$  mixtures, see Mitscherlich (22), Freyer and Meyer (23), Gautier and Hélier (24), Hélier (25), all according to method 1; Meyer, Krause, and Askenasy (26), Emich (1), Meyer and Münch (27) according to method 2, Fiesel (28) (method, 4), Wartenberg and Kannenberg (29) (method 5a).

TABLE 2.—IGNITION TEMPERATURE OF  $H_2$ , 0.5 SEC INDUCTION PERIOD  
[FROM DIXON (17)]

| $p$ , mm Hg | Ignition temperature $H_2$ in $O_2$ ,<br>° | Ignition temperature $H_2$ in air (for<br>comparison), ° |
|-------------|--|--|
| 75          | 500  | 502  |
| 100         | 512  | 515  |
| 150         | 533  | 536  |
| 200         | 550  | 553  |
| 250         | 563  | —  |
| 400         | 591  | 594  |
| 550         | 611  | —  |
| 760         | 625  | 630  |
| 1000        | 627  | —  |
| 2260        | 618  | —  |

Dixon and Crofts (5), according to method 3, find a constant rise of the ignition temperature with the increasing  $N_2$ . This can be conveniently stated in the following law: A mixture of  $2H_2 + O_2 + xN_2$  ignites at  $526 + 11x^\circ C$  (see Fig. 25). On the



(Entzündungstemperatur = ignition temperature)  
(in Luft = in air)

Fig. 26.—Ignition temperatures of CO in air. [From Prettre (4).]

other hand, experiments of Prettre according to method 2 show no such influence. In these experiments, a mixture

$2H_2 + O_2 + 4N_2$  ( $H_2$  in air stoichiometrically, 28.6 per cent  $H_2$ ) ignites at  $467^\circ$

a mixture

$2H_2 + O_2 + N_2$  ( $H_2$  in  $O_2 + N_2$  1:1 stoichiometrically 50 per cent  $H_2$ ) ignites at  $466^\circ$  (cf. Fig. 22, curves I and II)

Also, according to Goldmann (10) (method 5a), dilution with  $N_2$  does not change the ignition temperature of the  $H_2$ - $O_2$  mixture. The experiments of Mallard and Le Chatelier likewise resulted in the same ignition temperatures for stoichiometric  $H_2$ - $O_2$  and  $H_2$ -air mixtures.



If, instead of  $H_2$ , argon is added [Prettre (4)], the ignition temperature is again influenced negligibly, *e.g.*, a mixture composed of  $H_2 + O_2 + 4Ar$  ignited at  $473^\circ C$  (*cf.* Fig. 22, curve III). If, on the other hand,  $CO_2$  is substituted for atmospheric nitrogen, the ignition temperature is noticeably raised. According to Prettre, a mixture of  $2H_2 + O_2 + 4CO_2$  ignites at  $510^\circ$  (*cf.* Fig. 22, curve IV). Apparently, however, the  $CO_2$  does not act like an inert gas but rather takes part in the reaction in some way. Prettre reports that carbon formed on the walls of the container. Probably  $CO_2$  in the flame is reduced by H atoms. In addition, the flame has a different color and a different appearance.

Other authors also describe a raising of the ignition temperature of  $H_2$ - $O_2$  mixtures when  $CO_2$  is added. For example, Goldmann (10) finds under these conditions ignition temperatures of from  $590^\circ$  to  $660^\circ C$ , Bloch (8) for the theoretical mixture  $2H_2 + O_2 + 4CO_2$  finds  $625^\circ$ .

**Carbon Monoxide. Ignition Temperatures of CO and Air Mixtures.**—Older measurements by Mallard and Le Chatelier (2) yielded  $650^\circ C$  for mixtures with 30 per cent CO. Taffanel and Le Floch (3) found, according to method 2, for mixtures with 20 to 65 per cent CO content independent of the composition,  $610^\circ C$  in a container of  $350\text{ cm}^3$  volume, and  $700^\circ C$  in a container of  $9\text{ cm}^3$  volume. According to the same method, there are detailed studies of recent date by Prettre (4). The absolutely dry mixture ignites at temperatures of from  $654^\circ$  to  $730^\circ$  according to the composition (see Fig. 26). In CO mixtures, Prettre also finds considerable induction periods, the length of which decreases with rising temperature; *cf.*, for example, Table 3.

TABLE 3  
CO-air Mixture 32.4 per cent CO

| $t^\circ C$ | Induction period, sec | $t^\circ C$ | Induction period, sec |
|-------------|-----------------------|-------------|-----------------------|
| 655         | $\infty$              | 667         | 1                     |
| 658         | 4                     | 675         | 0.5                   |
| 660         | 2                     | 680         | Very small            |

Bloch (8) finds according to method 4a, for the mixture with 30 per cent CO,  $720^\circ C$  (*cf.* Fig. 27, curve a). McDavid (11), according to method 6, finds  $931^\circ$ .

If pure CO is mixed with  $O_2$  instead of with air, no essentially different ignition temperatures are observed. The following experimental data are available:

|  |                           |
|--|---------------------------|
| Mallard and Le Chatelier (Method 2), 15% CO..... | $630^\circ$ – $650^\circ$ |
| 30% CO.....                                      | $650^\circ$ – $680^\circ$ |
| 70% CO.....                                      | $645^\circ$ – $650^\circ$ |
| Dixon and Coward (31) (Method 4).....            | $637^\circ$ – $658^\circ$ |
| Goldmann (10) (Method 5a).....                   | $640^\circ$               |
| Bloch (8) (Method 4a), 70% CO.....               | $589^\circ$ (Fig. 27)     |

In the case of the last value, the great deviation from the ignition temperature of the theoretical CO-air mixture is due to the fact that the related CO showed a varying degree of purity. The ignition temperatures of CO mixtures depend a great deal on the purity of the gas. Small additions of  $H_2$ , water vapor, or similar hydrogen compounds lower the ignition temperature considerably, in contrast to pure mixtures. Dixon (30) had already observed that extremely dry  $CO$ - $O_2$  mixtures are considerably

more difficult to ignite than those with a small amount of moisture. The reasons for this are to be sought in the mechanism of the CO oxidation (see Chap. XI). Detailed experiments on the lowering of the ignition temperature of CO-air mixtures with an increasing  $\text{H}_2\text{O}$  content were conducted, for example, by Prettre, Dixon, and

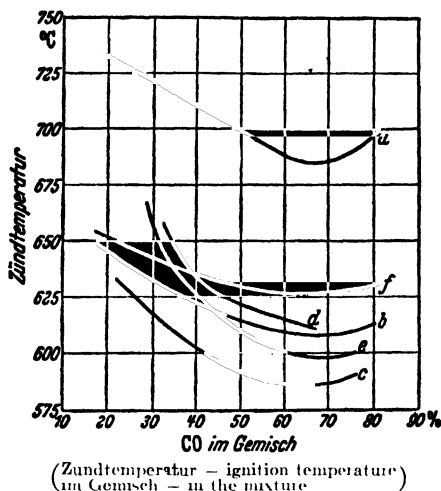


FIG. 27.—Ignition temperatures of various CO mixtures. *a*, CO in air (dry); (CO pure). *b*, CO in air (dry); (CO from steel flask, 1.5 per cent  $\text{H}_2$  content). *c*, CO in  $\text{O}_2$ . *d*, CO in  $\text{O}_2 + \text{CO}_2$  mixture ( $\text{O}_2:\text{CO}_2 = 0.21:0.79$ ). *e*, CO in  $\text{O}_2 + \text{CO}_2$  mixture ( $\text{O}_2:\text{CO}_2 = 1.1$ ). *f*, CO in air (wet) (CO pure). [From Bloch (8).]

Bloch. The results obtained by Prettre (1), according to method 2, are given by Table 4.

TABLE 4

|                             | % $\text{H}_2\text{O}$ in mixture |      |      |      |      |      |
|-----------------------------|-----------------------------------|------|------|------|------|------|
|                             | 0                                 | 1.50 | 2.25 | 3.20 | 4.15 | 5.60 |
| Mixture with 23.55% CO..... | 656                               | 618  | 639  | 630  | 632  | 633  |
| Mixture with 61.90% CO..... | 672                               | 652  | 640  | 641  | 641  | 642  |

For results of Dixon, see Fig. 28 (method 4). For the results of Bloch, see Fig. 27 (method 4a; moisture = 2.3 per cent  $\text{H}_2\text{O}$  in the mixture).

A small addition of  $\text{H}_2$  has a still greater influence on the ignition temperature of CO-air mixtures than a corresponding addition of  $\text{H}_2\text{O}$ . Prettre reports that an addition of 0.5 to 0.7 per cent  $\text{H}_2$  in a CO-air mixture suffices to lower the ignition temperature by more than 50 per cent. Dixon (see Fig. 29) obtains similar results. In a content of 25 per cent  $\text{H}_2$  (relative to CO), the curve is almost identical with that for the ignition of  $\text{H}_2$ -air mixtures.

For Bloch's results on the influence of a small  $\text{H}_2$  addition (CO "out of a steel bottle" is adulterated with 1.5 per cent  $\text{H}_2$ ), see Fig. 27.

Of interest is the discovery by Dixon that an addition of water vapor to CO-air mixtures that already contain a small amount of  $H_2$  raises the ignition temperature again, in other words, the influences are not cumulative (see Fig. 30). The influence

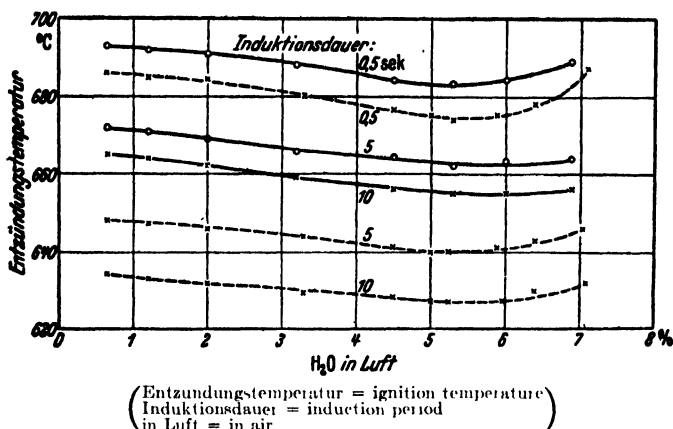


FIG. 28.—Ignition temperatures of CO in air with increasing  $H_2O$  content. (Solid line represents 760 mm total pressure; dashed line represents 400 mm total pressure.) [From Coward (17).]

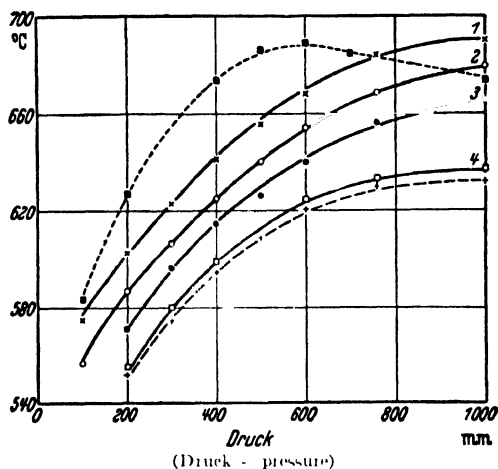


FIG. 29. Ignition temperatures of CO with varying  $H_2$  content in air. 1, CO with 1 per cent  $H_2$  in air (dry). 2, CO with 2 per cent  $H_2$  in air (dry). 3, CO with 5 per cent  $H_2$  in air (dry). 4, CO with 25 per cent  $H_2$  in air (dry). Dotted line, CO + 5.3 per cent  $H_2O$  in air (dry). Dashed line,  $H_2$  in air (dry). [From Coward (17).]

of larger amounts of hydrogen was investigated by Prettre (4), using method 2 ( $CO:H_2 = 1:1$  in various mixtures with air; cf. Fig. 31), and Bloch (8), according to method 4a (cf. Fig. 32).

Dilution of  $\text{CO-O}_2$  mixtures with other inert gases instead of nitrogen leads to a partial raising of the ignition temperature. For example, Bloch (8) (Fig. 27) finds that a  $\text{CO}_2$  addition raises the ignition temperature more than a corresponding addi-

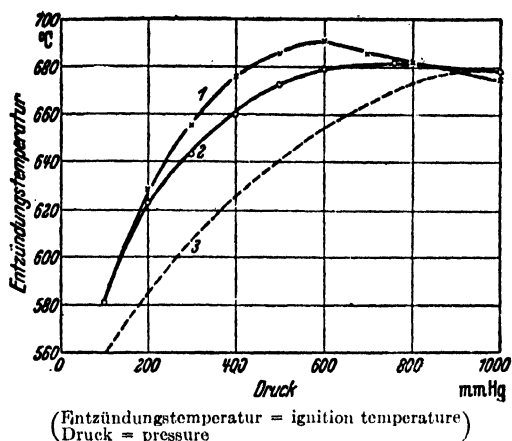


FIG. 30.—Ignition temperatures of CO with and without  $\text{H}_2$  in moist and dry air. 1, CO in air with 5.3 per cent  $\text{H}_2\text{O}$ . 2, CO with 2 per cent  $\text{H}_2$  in air with 5.3 per cent  $\text{H}_2\text{O}$ . 3, CO with 2 per cent  $\text{H}_2$  in air (dry). [From Coward (17).]

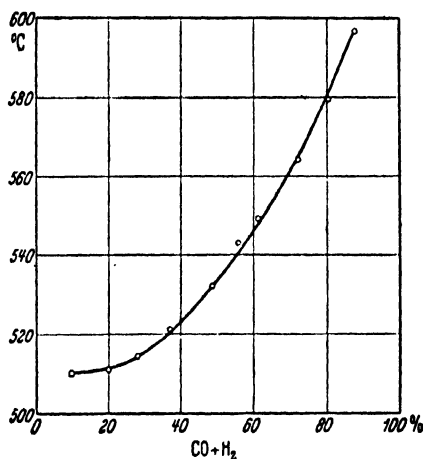
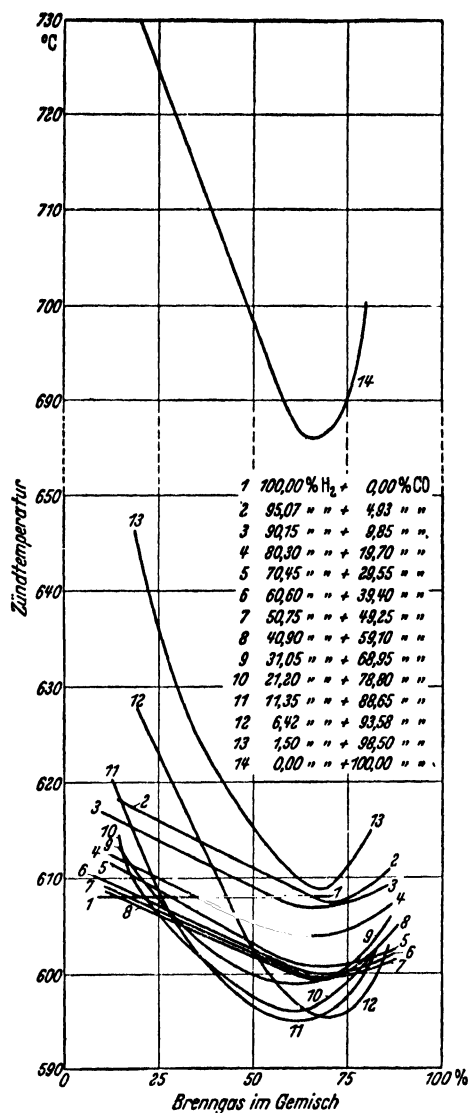


FIG. 31.—Ignition temperatures of  $\text{CO} + \text{H}_2$  mixture ( $\text{CO}:\text{H}_2 = 1:1$ ) in air. [From Prettre (4).]

tion of  $\text{N}_2$ . The same point is made by Mallard and Le Chatelier (2). A mixture of the composition 35 per cent  $\text{CO} + 15$  per cent  $\text{O}_2 + 50$  per cent  $\text{CO}_2$  did not ignite until  $695^\circ$  to  $715^\circ\text{C}$ .



(Zündtemperatur = ignition temperature  
Brenngas im Gemisch = fuel gas in the mixture)

Fig. 32.—Ignition temperatures of various CO + H<sub>2</sub> mixtures in air, dry. [From Bloch (8).]

Having shown in detail what influences the ignition temperatures are subject to for H<sub>2</sub> and CO, we present in Tables 5 to 8 a compilation of "ignition temperatures" of several important substances mixed with air at atmospheric pressure (unless otherwise indicated, according to Landolt-Börnstein).

TABLE 5

| Compound                      | % in mixture with air | Experimental method | Ignition temperature, ° | Compound               | % in mixture with air | Experimental method | Ignition temperature, ° |
|-------------------------------|-----------------------|---------------------|-------------------------|------------------------|-----------------------|---------------------|-------------------------|
| <i>Paraffin Hydrocarbons</i>  |                       |                     |                         | Benzol                 | 6                     | 2                   | 720                     |
| Methane                       | 2                     | 2                   | 850                     | Cyclohexane            | 1.5                   | 4a                  | 642                     |
| Methane                       | 4                     | 2                   | 810                     | Cyclohexane            | 6                     | 4a                  | 545                     |
| Methane                       | 8                     | 2                   | 806                     | Toluol                 | 2                     | 4a                  | 660                     |
| Ethane                        | 1.9                   | 2                   | 594                     | <i>Other Compounds</i> |                       |                     |                         |
| Ethane                        | 8.15                  | 2                   | 540                     | Diethyl ether          | 2                     | 2                   | 218                     |
| Propane                       | 1.25                  | 2                   | 588                     | Diethyl ether          | 5                     | 2                   | 205                     |
| Propane                       | 4.90                  | 2                   | 525                     | Diethyl ether          | 8                     | 2                   | 202                     |
| Butane                        | 1.25                  | 2                   | 569                     | Diethyl ether          | 17                    | 2                   | 204                     |
| Butane                        | 3.65                  | 2                   | 515                     | Diethyl ether          | 6.6                   | 3                   | 227                     |
| Butane                        | 7.65                  | 2                   | 489                     | Acetone                | 3.5                   | 2                   | 579                     |
| Pentane                       | 1.5                   | 2                   | 548                     | Acetone                | 9.9                   | 2                   | 561                     |
| Pentane                       | 2.75                  | 2                   | 520                     | Ethanol                | 3                     | 2                   | 525                     |
| Pentane                       | 7.65                  | 2                   | 476                     | Ethanol                | 5                     | 2                   | 500                     |
| Hexane                        | 2                     | 4a                  | 625                     | Ethanol                | 7                     | 2                   | 482                     |
| Hexane                        | 4                     | 4a                  | 592                     | Carbon disulphide      | 0.5                   | 2                   | 81                      |
| Hexane                        | 7                     | 4a                  | 630                     | Carbon disulphide      | 2                     | 2                   | 120                     |
| Hexane                        | 6.7                   | 3                   | 300 306                 | Carbon disulphide      | 4.5                   | 2                   | 148                     |
| Heptane                       | 4                     | 4a                  | 580                     | Carbon disulphide      | 8                     | 2                   | 198                     |
| Heptane                       | 5                     | 3                   | 280                     | Carbon disulphide      | 15                    | 2                   | 269                     |
| Heptane                       | 6.7                   | 3                   | 285                     | Carbon disulphide      | 25                    | 2                   | 316                     |
| Octane                        | 6.7                   | 3                   | 275                     | Carbon disulphide      | 30                    | 2                   | 323                     |
| <i>Unsaturated Solutions</i>  |                       |                     |                         | Carbon disulphide      | 12.5                  | 3                   | 253                     |
| Ethylene                      | 6                     | 4a                  | 600                     | Hydrogen sulphide      | 1                     | 2                   | 373                     |
| Ethylene                      | 10                    | 4a                  | 575                     | Hydrogen sulphide      | 3                     | 2                   | 335                     |
| Ethylene                      | 25                    | 4a                  | 540                     | Hydrogen sulphide      | 8                     | 2                   | 304                     |
| Acetylene                     | 10                    | 2                   | 500                     | Hydrogen sulphide      | 12                    | 2                   | 290                     |
| Acetylene                     | 20                    | 2                   | 400                     | Hydrogen sulphide      | 19.9                  | 2                   | 315                     |
| Acetylene                     | 45-55                 | 2                   | 335                     | Hydrogen sulphide      | 27                    | 2                   | 341                     |
| Acetylene with O <sub>2</sub> | 30                    | 1                   | 386                     | Hydrogen sulphide      | 40                    | 2                   | 400                     |
| Acetylene with O <sub>2</sub> | 80                    | 1                   | 352                     | Hydrogen sulphide      | 60                    | 2                   | 487                     |
| <i>Cyclical Compounds</i>     |                       |                     |                         | Light gasoline         | 2                     | 2                   | 565                     |
| Benzol                        | 2                     | 2                   | 770                     | Light gasoline         | 4                     | 2                   | 545                     |
| Benzol                        | 4                     | 2                   | 725                     | Light gasoline         | 6                     | 2                   | 535                     |

TABLE 6.—LOWEST MEASURED IGNITION TEMPERATURES OF SEVERAL IMPORTANT GASES IN MIXTURE WITH AIR AT ATMOSPHERIC PRESSURE

|                      |      |                        |      |
|----------------------|------|------------------------|------|
| Hydrogen.....        | 530° | Ethylene.....          | 540° |
| Carbon monoxide..... | 610° | Propylene.....         | 455° |
| Methane.....         | 645° | Butene.....            | 445° |
| Ethane.....          | 530° | Acetylene.....         | 335° |
| Propane.....         | 510° | Hydrogen sulphide..... | 290° |
| Butane.....          | 490° | Illuminating gas.....  | 560° |

TABLE 7.—THE INFLUENCE OF ANTIKNOCK COMPOUNDS ON THE IGNITION TEMPERATURE OF HYDROCARBONS

|  |      |
|--|------|
| <i>n</i> -Hexane, Method 2 without addition.....   | 338° |
| <i>n</i> -Hexane, Method 2 with 0.1% Fe(CO) <sub>5</sub> .....                           | 410° |
| <i>n</i> -Hexane, Method 2 with 1% Fe(CO) <sub>5</sub> .....                             | 456° |
| <i>n</i> -Hexane, Method 2 with 1% Pb(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> ..... | 487° |

TABLE 8.—RAISING THE IGNITION TEMPERATURE OF VARIOUS HYDROCARBONS BY THE ADDITION OF 0.25 VOLUME PER CENT  $\text{Pb}(\text{C}_2\text{H}_5)_4$  (ACCORDING TO METHOD 2)

|                 | Without addition | With addition |
|-----------------|------------------|---------------|
| Pentane.....    | 515              | 590           |
| Iso-hexane..... | 525              | 571           |
| Heptane.....    | 430              | 513           |

## REFERENCES

1. EMICH: *Mh. Chem.*, **21**, 1061 (1900).
2. MALLARD and LE CHATELIER: *Compt. rend.*, **91**, 825 (1880). Recherches expérimentelles et théoretiques sur la combustion des mélanges gazeux explosifs, Paris, 1883.
3. TAFFANEL and LE FLOCH: *Compt. rend.*, **156**, 1544 (1913); **157**, 469, 595, 714 (1913).
4. PRETTRE: *Ann. office nat. des combust. liquides*, **6**, 7, 269, 533 (1931).
5. DIXON and CROFTS: *J. Chem. Soc.*, **105**, 2036 (1914).
6. TIZARD: *Proc. NW Coast. Inst. Engng.*, **3**, 381 (1921).
7. HOLM: *Z. angew. Chem.*, **26**, 273 (1913).
8. BLOCH: Karlsruhe dissertation, 1934.
9. MOORE: *Chemistry & Industry*, **36**, 109 (1917); *Autom. Engr.*, **10**, 199 (1920).
10. GOLDMANN: *Z. physik. Chem.*, Sec. B, **5**, 316 (1929).
11. McDAVID: *J. Chem. Soc.*, **111**, 1003 (1917).
12. WHITE and PRICE: *J. Chem. Soc.*, **115**, 1248 (1919).
13. SILVER: *Phil. Mag.*, **23**, 633 (1937).
14. DAVY: *Ann. Phys. Chem.*, (II), **1**, 136 (1816); **4**, 260, 337 (1817).
15. COWARD and WHEELER: *Safety in Mines Research Board Paper* 53.
16. COWARD and GUEST: *J. Am. Chem. Soc.* **49**, 2479 (1927).
17. COWARD (research by Dixon): *J. Chem. Soc.*, 1934 (II), p. 1382.
18. FALK: *Ann. Physik*, (IV), **24**, 450 (1907); *J. Am. Chem. Soc.*, **28**, 1517 (1906); **29**, 1536 (1907).
19. CASSEL: *Ann Physik*, **51**, 685 (1916).
20. DIXON, BRADSHAW, and CAMPBELL: *J. Chem. Soc.*, **105**, 2027 (1914).
21. TIZARD and PYE: *Phil. Mag.*, (VI), **44**, 79 (1922); (VII), **1**, 1094 (1926).
22. MITSCHERLICH: *Ber. deut. chem. Ges.*, **26**, 160, 399 (1893).
23. FREYER and MEYER: *Ber. deut. chem. Ges.*, **25**, 622 (1892).
24. GAUTIER and HÉLIER: *Compt. rend.*, **122**, 566 (1896).
25. HÉLIER: *Ann. chim. phys.*, **10**, 521 (1897).
26. KRAUSE and MEYER: *Liebigs Ann. Chem.*, 1891, p. 85. ASKENASY and MEYER: *Liebigs Ann. Chem.*, 1892, p. 49. MEYER: *Ber. deut. chem. Ges.*, **26**, 428 (1893).
27. MEYER and MÜNCH: *Ber. deut. chem. Ges.*, **26**, 2421 (1893).
28. FIESEL: *Z. physik. Chem.*, **97**, 158 (1921).
29. VON WARTENBURG and KANNENBERG: *Z. physik. Chem.*, **105**, 205 (1923).
30. DIXON: *Brit. Ass. Advancement Sci. Rept.* 503; *Phil. Trans. Roy. Soc. London*, A, **175**, 617 (1884).
31. DIXON and COWARD: *J. Chem. Soc.*, **95**, 514 (1909).

## CHAPTER II

### SPARK IGNITION I: THERMAL THEORY OF SPARK IGNITION

**1. Basic Facts and Statement of the Problem.**—If a spark is sent through an explosive gas mixture, it can cause general ignition. In this case, the transformation continues in a flame proceeding from the spark. Whether ignition occurs or not depends in a given gas mixture on the intensity of the spark and, in addition, on details of the spark discharge, *e.g.*, the time factor in the current and voltage of the spark discharge, the distance between the electrodes, and other influences. In general, in spark ignition, as well as in most spontaneous explosions, we are not dealing with a pure thermal process; for almost always chain reactions and chain-branchings play a role. Under certain circumstances, even electrical processes enter in.<sup>1</sup> It is convenient first of all to select from the many possibilities those phenomena which can be explained by purely thermal processes even in borderline cases. Furthermore, we must take into account the fact that diffusion processes play a role when chain reactions are introduced and that they follow the same formal laws as the heat-conduction phenomena treated here. The formal relations deduced on the basis of a pure theory of heat will therefore not necessarily lose their validity in the more general case. Since, in addition, the thermal effect probably plays a role in each spark, the treatment of this borderline case is at any rate logical.

In this chapter, then, we shall be interested only in how much thermal energy has been produced by the spark, and we shall consider important the way in which this production of energy is divided in space and time. Thus, we have the following problem: In a volume element of given size, a definite quantity of heat has been produced during a given time. We ask:

1. When does a rapid combustion develop in this volume element?
2. How does combustion spread from this element; or, rather, when does it spread, if at all, leading to general ignition?

Obviously, if the entire gas is to be ignited, the spark volume must necessarily explode; but it does not at all follow that this condition is sufficient. One could at any rate imagine that a very small volume would

<sup>1</sup> EMÉLEUS, K.G., R.W. LUNT, and C.A. MEEK, *Proc. Roy. Soc. London*, A, **156**, 394 (1936). EMÉLEUS, K.G., and R.W. LUNT, *Trans. Faraday Soc.*, **32**, 1504 (1936). LUNT, R.W., *Trans. Faraday Soc.*, **32**, 1691 (1932). LUNT, R.W., C.A. MEEK, and E.C.W. SMITH, *Proc. Roy. Soc. London*, A, **158**, 729 (1937). LUNT, R.W., and C.A. MEEK, *Proc. Roy. Soc. London*, A, **157**, 146 (1926).



explode but that the heat from it would dissipate by conduction more rapidly than the neighboring layers could follow the explosion. Indeed, there is a series of experiments proving this (*cf.*, for example, the experiments by Coward and Meiter as well as by Holm, discussed on pages 57ff.).

No completely satisfactory theoretical treatment of spark ignition exists in the literature up to the present. If the condition is arbitrarily imposed that a definite minimum volume be heated to an "ignition temperature" by the spark, it can be easily indicated what amounts of energy ought to be added by pointlike sources, assumed spatially momentarily, or sources lasting over a certain period of time. Qualitatively very reasonable results are obtained (*cf.*, for example, Coward and Meiter, page 98).

In connection with our remarks on thermal explosion and ignition by heated surfaces, we could proceed first of all according to the following computation.

The spark volume in which a thermal explosion takes place is considered by itself, and the heat of reaction can be conducted off by the assumed surrounding cold gas. Since the heat conduction, other conditions being equal, is directly proportional to the temperature drop and since this is approximately inversely proportional to the radius of the container, the heat conduction in a spark volume of about 0.01 cm radius will be about a thousandfold greater than in a reaction vessel of 10 cm radius. Hence the production of heat for ignition, *i.e.*, the velocity of reaction, would probably have to be increased by about a thousand. Let us assume that the normal "ignition temperature" amounts to 600°C and the "heat of activation" of the reaction is about 35 kcal; for an increase of the reaction velocity by a thousand, a temperature rise of about 450° (to about 1320° abs) would be necessary. The smaller the "spark volume" the higher the necessary temperature. That is identical with what we have seen in the ignition by injected hot spheres (*cf.* pages 30ff.).

To be sure, this is only a very rough approximation which is inadequate for other reasons than that it does not take into account reactions with chain-branching. To be sure, it indicates that much higher energies per unit of volume are necessary for ignition in the spark than in large spaces, but it leaves entirely untouched the problem of how and whether explosion spreads from the small volume. One can treat this problem exactly only if one has the theory of flame propagation at one's command. We shall come back to this later. To a certain extent, the necessary considerations are, to be sure, already implicit in the statements above. If the spark volume explodes with simultaneous heat conduction, it means that the area surrounding the spark is progressively heated by

conduction. From this fact, however, the following is clear. For the spread of conduction, not only the primary origin of the explosion in the center of the spark plays a role, but also the heat production by the progressively explosive combustion, the velocity of which must decrease again with increasing conversion. The quantitative treatment of the processes is further complicated by the following phenomenon. Let us assume the rather short time of about  $10^{-4}$  sec from the appearance of the spark until the complete development of the explosive combustion in it (the "spark diameter" is about  $2 \cdot 10^{-2}$  cm). During this short interval, gas molecules from the territory surrounding the spark have been displaced, the average square of which is given by

$$\overline{\Delta x^2} = 2Dt \quad (1)$$

where  $t$  is the time and  $D$  the diffusion coefficient, let us say of the order of magnitude of  $1 \text{ cm}^2/\text{sec}$ . For  $\sqrt{\overline{\Delta x^2}}$ , we obtain with  $t = 10^{-4}$  sec about  $10^{-2}$  cm. That means that, during the time of  $10^{-4}$  sec assumed necessary for the development of the explosion, considerable quantities of fresh gas have been diffused into the spark (and corresponding masses of burning and burned gases have been diffused out of the spark). An exact treatment of spark ignition would accordingly be impossible without considering diffusion. One would therefore have to have (1) a differential equation for the temperature change by conduction and reaction and (2) a differential equation for the concentration change by diffusion and reaction, and (3) in both it would be necessary to consider the equation for the chemical transformation at every place that had been influenced by the changes in temperature and concentration following out of (1) and (2). The problem is so complicated that an exact treatment is excluded from the start. We shall therefore always disregard diffusion, and any effects caused by it will be added merely as supplementary corrections.

**2. Expressions for a Simplified Quantitative Treatment.**—Disregarding the factors indicated above, we should proceed as follows in giving the differential equations for spark ignition. The temperature change with time in the proximity of the spark is given in the first place by heat conduction, and further by the heat produced as a result of conversion. The usual equation for heat conduction is<sup>1</sup>

$$c\sigma \frac{\partial T}{\partial t} = \text{div} (k \text{ deg } T) \quad (2)$$

in which  $c$  is the specific heat (per unit of mass, not per mol),  $\sigma$  the density,  $T$  the temperature,  $t$  the time, and  $k$  the heat conductivity. For a con-

<sup>1</sup> Cf. textbooks on theoretical physics or Frank-Mises, "Differential- und Integralgleichungen der Physik," Brunswick, 1930/35 (cf. also below p. 117).

stant  $k$ , which we wish to assume in the following (but which is only a poor approximation to reality on account of the great differences in temperature), this is simplified to

$$c\sigma \frac{\partial T}{\partial t} = k \Delta T = k \left( \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) \quad (3)$$

if we use a rectangular system of coordinates.

In case  $-dn/dt = f(n) \exp(-E/RT)$  is the velocity of reaction,  $Q$  the heat quantity related to the corresponding transformation, then the analogous heating equation already given in the previous chapter (p. 11) holds

$$\bar{c} \frac{\partial T}{\partial t} = Qf(n) \exp\left(-\frac{E}{RT}\right) \quad (4)$$

In this,  $\bar{c}$  is the mean heat capacity which is related to the same unit of mass as the heat of reaction  $Q$ . The same thing holds for the constancy of  $c$  as held for that of  $k$ . As in the previous chapter, we introduce the quotient  $Q/c = T_m - T_0 = \Theta_m$ , the maximum rise in temperature which is possible by transformation, and write instead of (4)

$$\frac{\partial T}{\partial t} = \Theta_m f(n) \exp\left(-\frac{E}{RT}\right) \quad (5)$$

$f(n)$ , the factor of concentration of the velocity of reaction must, independent of more exact assumptions about the latter, have the effect of causing the velocity to equal zero in complete conversion (*i.e.*, conversion leading to equilibrium). As the simplest corresponding expression one can choose

$$f(n) \cong A(T_m - T) = A[\Theta_m - (T - T_0)] \quad (6)$$

for, in complete conversion,  $T = T_m$  and therefore  $f(n) = 0$ . If we define  $A$  so that the correct velocity of reaction results for  $t = 0$ , then we have at least a convenient expression that gives correctly the velocity of heating at both limits. It must be remembered, to be sure, that (5) and (6) are valid only as long as no addition or loss of heat occurs by conduction, since in that case the maximum temperature is not given any longer by  $T_m - T_0 = Q/\bar{c}$ . If, on the other hand, diffusion is taken into account, it would constantly supply new fresh gas to the zone of the spark, in other words decreasing the change of concentration with time. We shall write for (5)

$$\frac{\partial T}{\partial t} = \mu \exp\left(-\frac{E}{RT}\right) \quad (7)$$

in which we shall reserve the right to substitute for  $\mu$  a suitable average value according to the foregoing.

If we write the heat-conduction equation (3)<sup>1</sup>

$$\frac{\partial T}{\partial t} = \kappa \Delta T \quad (8)$$

with  $\kappa$ , the thermometric conductivity (diffusivity) given by

$$\kappa = \frac{k}{c\sigma} \quad (9)$$

the resulting heating equation becomes

$$\frac{\partial T}{\partial t} = \kappa \Delta T + \mu \exp \left( -\frac{E}{RT} \right) \quad (10)$$

We must now choose the proper distribution of initial temperature in the spark and then investigate how this temperature changes according to (10). An ignition will propagate itself only if the temperature constantly rises in the spark and its proximity.

In order to get a comprehensive view of the conditions, let us consider the one-dimensional case, with heat conduction only in the direction of the  $x$ -axis, where we must imagine the spark as perhaps a flat disk at the zero point in the system of coordinates perpendicular to the  $x$ -axis and likewise to a nonconducting tube extending in the  $x$ -direction. Equation (10) then becomes

$$\frac{\partial T}{\partial t} = \kappa \frac{\partial^2 T}{\partial x^2} + \mu \exp \left( -\frac{E}{RT} \right) \quad (11)$$

$\kappa$ , the thermometric conductivity, for air at 500°C (which we shall consider the average temperature) is about 1 cm<sup>2</sup>/sec. For the reaction velocity, we assume  $\sim 3 \cdot 10^9 \exp (-40,000/RT)$ . (This corresponds approximately to the reaction velocity of iodine with hydrogen at atmospheric pressure.) As the maximum temperature reached, we assume about 3000°. Let the initial temperature be 0°C. Then we get

$$\mu \cong 3000 \cdot 3 \cdot 10^9 \cong 10^{13} \quad (12)$$

And so

$$\frac{\partial T}{\partial t} \cong \frac{\partial^2 T}{\partial x^2} + 10^{+13} \cdot 10^{-8750/T} \quad (13)$$

Since the spark needs a certain time to build up, during which a definite conversion can already have taken place, it is practical to choose a distribution of temperature not for  $t = 0$ , but for a point of time corresponding to the building up of the discharge. For this, we shall assume

<sup>1</sup>  $\Delta T$  here means the Laplacian differential equation (3).

for the moment  $t_0 = 10^{-4}$  sec.<sup>1</sup> For a distribution of temperature, we choose one that is the solution of the heat-conduction equation without heating by reaction, in other words, the equation<sup>2</sup>

$$\frac{\partial T}{\partial t} = \kappa \frac{\partial^2 T}{\partial x^2} = 1 \frac{\partial^2 T}{\partial x^2}$$

And we choose a solution to which an initial distribution for  $t = 0$  corresponds, as in Fig. 33. For  $t = 0$  and  $|x| > \alpha$ , let  $\Theta = (T - T_0) = 0$ ; for  $-\alpha \leq x \leq +\alpha$ , let  $\Theta = (T - T_0) = T_1$ . One solution of (13) satisfying this initial condition is<sup>3</sup>

$$\Theta = \frac{T_1}{2} \left[ \psi \left( \frac{\alpha - x}{2a\sqrt{t}} \right) + \psi \left( \frac{\alpha + x}{2a\sqrt{t}} \right) \right] \quad (14)$$

in which  $a$ , the square root of the thermometric conductivity,  $a = \sqrt{\kappa}$ , in our case = 1.

Therefore

$$\Theta = \frac{T_1}{2} \left[ \psi \left( \frac{\alpha - x}{2\sqrt{t}} \right) + \psi \left( \frac{\alpha + x}{2\sqrt{t}} \right) \right] \quad (15)$$

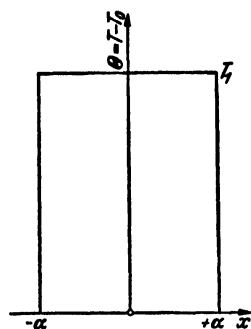


FIG. 33.—Temperature distribution for  $t = 0$ ; compare the text.

$\psi(\xi)$  represents the integral of error

$$\psi(\xi) = \frac{2}{\sqrt{\pi}} \int_0^\xi e^{-\eta^2} d\eta \quad (16)$$

which is tabulated, for example, in Jahnke-Emde.<sup>4</sup> With  $T_1 = 1000^\circ\text{C}$ , and  $\alpha =$  as the case may be,  $1, 2, 3, 4 \cdot 10^{-2}$  cm, we get, for example, the curves of Fig. 34, in which the curves I, II, III, IV refer to  $\alpha = 10^{-2}, 2 \cdot 10^{-2}, 3 \cdot 10^{-2}$ , and  $4 \cdot 10^{-2}$  cm. The maximum temperatures  $\Theta$  for  $x = 0$  are, in their order  $520.5^\circ, 842.7^\circ, 966.1^\circ$ , and  $995.3^\circ\text{C}$  for  $t = 10^{-4}$  sec. After a further  $10^{-5}$  sec (in other words, for  $t = 1, 1 \cdot 10^{-4}$  sec), these temperatures have dropped to  $499.2^\circ, 922.5^\circ, 956.9^\circ$ , and  $992.9^\circ$ , as long as only heat conduction is considered. Thus there would result for

$$\left( \frac{\partial T}{\partial t} \right)_{\text{cond}} \cong \left( \frac{\Delta T}{\Delta t} \right)_{\text{cond}}$$

at the zero point of the system of coordinates (*i.e.*, in the center of the spark) the following:

Temperature change by conduction  $(\Delta T)_{\text{cond}}$  during  $10^{-5}$  sec as well as

<sup>1</sup> Since we have the choice of the zero point for the computation of time, we are not being arbitrary.

<sup>2</sup> Again with the special value  $\kappa \cong 1 \text{ cm}^2/\text{sec}$ .

<sup>3</sup> Cf., *e.g.*, Frank-Mises, cited on p. 49.

<sup>4</sup> Jahnke-Emde, "Tables of Functions."

$\left(\frac{\Delta T}{\Delta t}\right)_{\text{cond}} \cong \left(\frac{\partial T}{\partial t}\right)_{\text{cond}}$  with  $x = 0$  for the example of the text in the cases:

|   | I     | II    | III   | IV                 |
|---|-------|-------|-------|--------------------|
| $(\Delta T)_{\text{cond}}, ^\circ\text{C} \dots\dots\dots$              | -21.3 | -20.2 | -9.2  | -2.4               |
| $(\partial T/\partial t)_{\text{cond}}, \text{deg/sec} \dots\dots\dots$ | -2.13 | -2.02 | -0.92 | $-0.24 \cdot 10^6$ |

We continue with the increases in temperature computed according to the expression for reaction velocity and resulting from the heat of reaction.

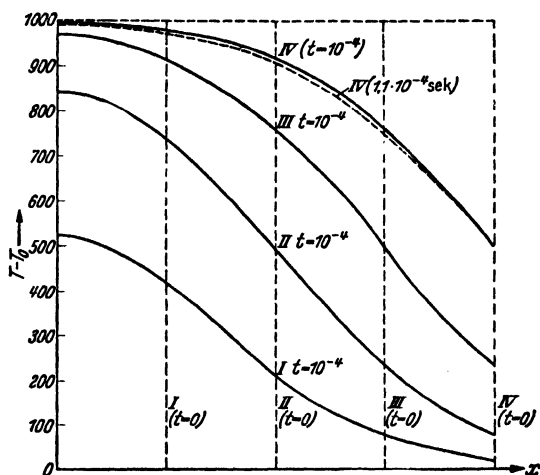


Fig. 34.—Temperature distribution for  $t = 10^{-4}$  sec at various initial distributions; compare the text.

Temperature increases by chemical reaction  $(\Delta T/\Delta t)_{\text{react}} \cong (\partial T/\partial t)_{\text{react}}$  in the above cases result as follows:

|  | I       | II                | III                | IV                 |
|--|---------|-------------------|--------------------|--------------------|
| $\Theta, ^\circ\text{C} \dots\dots\dots$                                 | 520.5   | 842.7             | 966.1              | 995.3              |
| $(\partial T/\partial t)_{\text{react}}, \text{deg/sec} \dots\dots\dots$ | $+10^2$ | $+1.4 \cdot 10^3$ | $+0.85 \cdot 10^6$ | $+1.25 \cdot 10^6$ |

From this it can be seen that only in Case IV does heating by chemical reaction exceed cooling by conduction when  $x = 0$ . In Cases I to III (spark radius  $\leq 3 \cdot 10^{-2}$  cm), ignition certainly does not take place. In order to decide the question as to whether ignition takes place in Case IV, a more exact investigation is necessary. We therefore give the temperature values of IV for  $t = 10^{-4}$  and  $1.1 \cdot 10^{-4}$  sec for various distances from the center of the spark.

TEMPERATURES IN CASE IV

| $x$ , cm.....                            | 0     | $10^{-2}$ | $2 \cdot 10^{-2}$ | $3 \cdot 10^{-2}$ | $4 \cdot 10^{-2}$ |
|--|-------|-----------|-------------------|-------------------|-------------------|
| $\theta$ , °C:                           |       |           |                   |                   |                   |
| For $t = 10^{-4}$ sec.....               | 995.3 | 982.8     | 921.4             | 760.3             | 500.0             |
| For $t = 1.1 \cdot 10^{-4}$ sec.....     | 993.1 | 978.1     | 911.4             | 749.6             | 500.0             |
| $(\Delta\theta)_{\text{cond}}$ , °C..... | -2.2  | -4.7      | -10.0             | -10.7             | 0                 |
| $(\Delta\theta)_{\text{reac}}$ , °C..... | 12.5  | 10.7      | 4                 | 0.3               | Minus             |

Let us first of all be clear about the following: If, for  $x = 0$ , heat production and heat conduction are balanced in the first moment, then this fact is not by any means sufficient for obtaining a static condition (in contrast to the conditions for thermal explosion; Chap. I, page 7). If (Fig. 35) the initial distribution is given by curve I (for  $t = 10^{-4}$  sec), curve II would be reached after the short time  $\Delta t$  without reaction. If, when  $x = 0$ , heat production is just large enough to compensate for conduction, it will not necessarily be true for  $x \leq 0$ . Under the influence of reaction, the dotted curve in Fig. 35

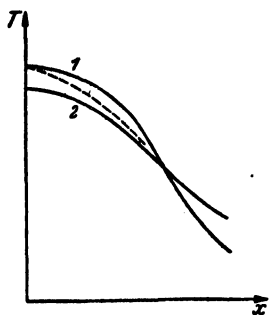


FIG. 35.

could result, i.e., when  $x = 0$ , the temperature has remained constant for the time being, the bend in the curve for temperature distribution and so also  $\partial^2 T / \partial x^2$  and heat conduction have however increased; in the following time element the temperature would therefore drop. Conditions prevailing in Fig. 36 would definitely lead to ignition. Curves 1 and 2 are intended to show the same as in Fig. 35. Let the heating be increased, however, until at the point  $x = x_0$  the heat of reaction surpasses conduction; the dotted curve would then result. As is indicated by the shaded portion, the temperature for all values of  $x$  has risen and would continue to do so (always disregarding the decreasing concentration as a result of the reaction).

Probably the conditions, as expressed in Fig. 36, are more than sufficient; for a case such as Fig. 37 could be imagined in which, to be sure, in a certain field of  $x < x_0$  the temperature at first falls but in which the integrated heat production from  $x = 0$  to  $x = x_0$  exceeds the heat conducted from the same field, and in which, by means of the heat production increasing in the region of  $x = 0$ , so much heat is furnished to the field with initially excessive conduction that the temperature finally rises in all directions (curves 3 and 4). Case IV, graphed in Fig. 34 and explained in the other tables, now stands just between the examples indicated by Figs. 36 and 37. It is therefore to be assumed that it comes quite close to the critical ignition limit. For more exact results, it would be

Probably the conditions, as expressed in Fig. 36, are more than sufficient; for a case such as Fig. 37 could be imagined in which, to be sure, in a certain field of  $x < x_0$  the temperature at first falls but in which the integrated heat production from  $x = 0$  to  $x = x_0$  exceeds the heat conducted from the same field, and in which, by means of the heat production increasing in the region of  $x = 0$ , so much heat is furnished to the field with initially excessive conduction that the temperature finally rises in all directions (curves 3 and 4). Case IV, graphed in Fig. 34 and explained in the other tables, now stands just between the examples indicated by Figs. 36 and 37. It is therefore to be assumed that it comes quite close to the critical ignition limit. For more exact results, it would be

necessary to follow the temperature development in space and time by further numerical computations.

If one designates the radial width of the temperature curve at  $t = 10^{-4}$  sec as the "spark diameter," a spark diameter of about 0.8 mm would be necessary for ignition.

If we now proceeded from the one-dimensional to three-dimensional heat flow corresponding to actual conditions, the conditions for ignition

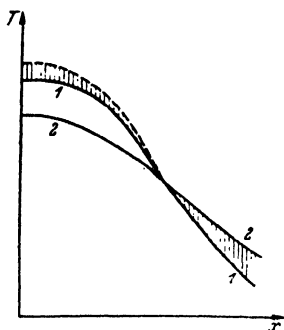


FIG. 36.

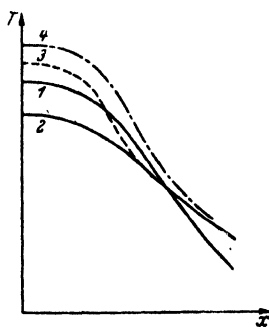


FIG. 37.

would naturally become somewhat less favorable. In place of the equation for heat conduction

$$\frac{\partial T}{\partial t} = \kappa \frac{\partial^2 T}{\partial x^2}$$

the following equation is needed for spherical symmetry in a three-dimensional case:

$$\frac{\partial T}{\partial t} = \kappa \left( \frac{\partial^2 T}{\partial r^2} + \frac{2}{r} \frac{\partial T}{\partial r} \right) \quad (17)$$

in which  $r$  is the distance from the center of the sphere.

Since  $\partial T / \partial r$  is negative, the second member represents added heat conduction. If, for example, the first member  $\partial^2 T / \partial r^2$ , similar to the examples above, represents a cooling velocity of

$$\left( \frac{\partial T}{\partial t} \right)_I \cong -10^5 \text{ deg/sec}$$

then, with  $r = 10^{-2}$  cm and a temperature drop of  $\sim 100^\circ$  per  $10^{-2}$  cm, as is also the case in the examples above, the second member once more contributes to the amount of

$$\left( \frac{\partial T}{\partial t} \right)_{II} \cong -2 \cdot 10^5 \text{ deg/sec}$$

i.e., the total conduction can be increased several times, but nothing would be changed in the order of magnitudes and in the qualitative picture. Correspondingly, one will either have to heat a predetermined



volume higher or bring a greater volume to a predetermined temperature if ignition is to result. Since solutions for heat-conduction equations in three-dimensional cases exist (*cf.* Frank-Mises, cited on page 49), the numerical computations for one-dimensional cases can also be applied to three-dimensional cases.

If we assume that the spark diameter is about double that given above, or 1.5 mm—which might actually be the case—the energy conducted in the spark would be  $\sim 10^{-3}$  cal. That is actually an amount that comes into consideration practically and has been assumed by Taylor-Jones, Morgan, and Wheeler<sup>1</sup> in computations for the heat diffusion of energy conducted in a spark in various ways.<sup>2</sup>

**3. Discussion of Experiments on Spark Ignition from the Standpoint of the Theory of Heat.**—Ignition by sparks, as we have emphasized again and again, cannot be understood exclusively as a thermal phenomenon. But it will be well to learn about a number of experiments and to discuss the attempt to explain them on the basis of the theory of heat (in borderline cases). The experiments and theories considered with the non-thermal part of the process are to be treated later (Chap. X). It appears<sup>3</sup> that we may take over the formulation originating with Taylor-Jones, Morgan, and Wheeler<sup>1</sup> as long as we are interested not in understanding the processes taking place in the spark during the discharge but only in whether general ignition results or not, namely, that the general ignition of a mixture depends on which volume of gas has been ignited by the spark first. However, the statement by the same authors, that it depends only on which volume of gas has been heated to ignition temperature by the thermal effect of the spark (*cf.* Chap. X) is not tenable. That this is no reasonable formulation is clear, among other things, from the fact that, according to our discussion above, there can be no universal ignition temperature for a small component volume of a gas. From a purely thermal point of view, it is to be expected—and all experiments corroborate this—that the general ignition of a mixture depends not only on the total energy introduced by a spark, but also on how this energy is introduced, whether by a very brief condenser discharge or by a longer oscillating discharge in a system with self-induction. In this case, it also depends on the frequency of the spark. Taylor-Jones, Morgan, and Wheeler<sup>1</sup> have attempted (by the inadmissible introduction of an igni-

<sup>1</sup> TAYLOR-JONES, E., J.D. MORGAN, and R.V. WHEELER, *Phil. Mag.*, (6), **43**, 359 (1922).

<sup>2</sup> Morgan determined that a spark with  $0.9 \cdot 10^{-3}$  cal is needed for ignition of methane-air mixtures with 8.8 per cent methane.

<sup>3</sup> *Cf.* in this connection the collective review of the author, *Z. Elektrochem.*, **41**, 183 (1935); particularly pp. 185ff. and the works listed there.

<sup>4</sup> TAYLOR-JONES, E., J.D. MORGAN, and R.V. WHEELER, *Phil. Mag.*, (6), **43**, 359 (1922). TAYLOR-JONES, A., *Phil. Mag.*, (7), **6**, 1090 (1928).

tion temperature) to arrive at quantitative formulations. If we use the known integrals of the formulas for heat conduction<sup>1</sup> for cases in which heat is either introduced at one point or extended over a small spherical volume, and in which, further, the heat is added either instantaneously or over a certain finite time, we can see that a predetermined minimum volume can be brought to "ignition temperature" with the smallest quantity of energy, if the addition of heat takes place instantaneously. We shall see later, however (*cf.* Chap. X), that the discharges of shortest duration are not the most effective for ignition under all conditions.

Even though it is clear from a purely thermal point of view that ignition does not depend only on the gross supply of energy, the actually observed details are understandable only if one observes the minute details of discharge, the excitation dissociation, and the ionization processes of the gas molecules. All this will be discussed under chain reactions. If one wishes to understand the whole process, from the origin of the explosion in the spark volume to the fully developed flame, a knowledge of the processes prevailing in flame propagation is, as has been mentioned, necessary. If explosion has occurred in a very small component volume, it propagates at first not with the normal velocity of combustion but at a much slower rate. This is called "delayed ignition" and will be discussed in the next chapter.

Coward and Meiter<sup>2</sup> have made a careful investigation of the ignition of methane-air mixtures by sparks and have discussed them from the thermal point of view. They have determined not only when ignition takes place but also what chemical effects are caused by sparks not yet sufficing for ignition. Methane was naturally chosen for the experiment because its ignition is especially dangerous from chance sparks in mines threatened by firedamp. Coward and Meiter used a reaction vessel with platinum electrodes (either at a fixed distance or at a distance adjustable by means of a screw). It was possible to measure the pressure or, more specifically, the pressure changes in the reaction vessel. In addition, gas analyses could be carried out. Sparks were caused either by the discharge of a condenser (with a capacity up to 0.0006  $\mu$ f) or by an inductor. Of all methane-air mixtures, those with 8 to 9 per cent methane ignite most easily by sparks. With the special apparatus equipped with platinum electrodes, with a gap of 0.52 mm, a primary current of 1.45 amp in the inductor sufficed for ignition. In a primary current of 1.40 amp, it was possible to send thousands of sparks through the mixture without ignition. From the analysis at the conclusion of the experiments, it was shown that a methane consumption per spark had

<sup>1</sup> *Cf.* FRANK-MISES, cited on p. 49.

<sup>2</sup> COWARD, H.F., and E.G. MEITER, *J. Am. Chem. Soc.*, **49**, 396 (1927).

taken place that corresponded to the complete reaction of a volume of 0.59 mm<sup>3</sup>. In other words, an appreciable volume of the mixture can be brought to combustion by a spark without causing general ignition.

In another series of experiments using the same distance between electrodes, the (primary) minimum strength of current necessary for ignition was 1.3 amp. At 1.25 amp, an average volume of 0.53 and 0.52 mm<sup>3</sup> per spark was converted (in the repeated experiment). If the distance between the electrodes was increased to 1.0, the required ignition current fell to 0.90 amp. At 0.85 amp, the average volume of gas converted was 0.45 or 0.41 mm<sup>3</sup>. Thus a much smaller decrease in the volume of gas converted per spark corresponds to a considerable drop in the required primary ignition current. The results can be understood without great difficulty if the smaller cooling effect of the more widely separated electrodes is taken into account.

Of interest also are the experiments with mixtures of varying methane content and a constant distance between electrodes of 0.52 mm. In Table 9, a selection from the experimental data of Coward and Meiter is given.

TABLE 9.—IGNITION EXPERIMENTS ON METHANE AND AIR MIXTURES (FROM COWARD AND MEITER)

|   |      |      |       |
|---|------|------|-------|
| Methane in mixture, %.....  | 6.22 | 8.49 | 11.18 |
| Primary current necessary for ignition, amp.....                      | 2.40 | 1.45 | 2.80  |
| Current intensity in the following experiment (without ignition)..... | 2.35 | 1.40 | 2.75  |
| Volume of the mixture burned per spark, mm <sup>3</sup> .....         | 1.40 | 0.59 | 1.01  |

From this, as has been noted again and again, it is clear that the farther one departs from the optimum mixture, the greater must be the energy expended for ignition. The volume of gas that can be consumed before ignition sets in thus rises sharply, as does also the required ignition current, when less ignitable mixtures are used. These mixtures are, at the same time, those which show lower flame velocities. For that reason, the results are also interesting in respect to the transition of the explosion to the fully developed flame in small component volumes; *cf.* the following chapter.

In Fig. 38 (after Wheeler) are given the minimum strength of ignition current (primary) for a number of hydrocarbon-air mixtures, which rise very systematically according to the ignition limits.

Experiments on the conversion by sparks of the same strength in mixtures of varying methane content, including those in which a flame is not able to propagate itself (the ignitable mixtures of methane and air lie about in the neighborhood of 5 to 13 per cent methane) are also

instructive. In the series of experiments in question and under the same conditions as above (electrode gap of 0.52 mm), a primary current of 1.50 amp was applied, except in the experiment with 8.49 per cent methane, where the primary current had to be reduced to 1.40 amp, since ignition would otherwise have taken place. The results are given in Table 10.

Even though the experiments show no definite regularity (at 11.18 per cent methane, we suspect an experimental error), it is possible to recognize no characteristic difference between the explosive and the

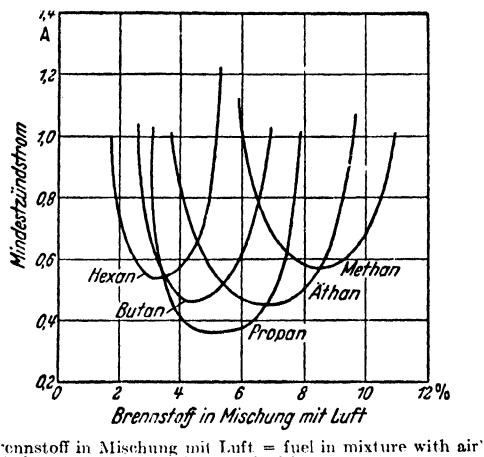


FIG. 38.—Minimum ignition-current intensities (in the primary circuit) for various hydrocarbon and air mixtures according to Wheeler. (From Bone-Townend, "Flame and Combustion.")

nonexplosive mixtures. The process within the spark itself does not differ very much in either case. The only difference is that in one case the forced conversion can spread to the outside and in the other case it cannot.

The sparks used, as shown by direct photography on a rotating drum (except with currents only 0.5 amp in strength), consisted of a considerable number of oscillations. The total duration was several thou-

TABLE 10.—CONVERSION DURING THE PASSAGE OF THE SPARK THROUGH METHANE AND AIR MIXTURES OF VARIED COMPOSITION (INCLUDING THOSE LYING OUTSIDE THE IGNITION LIMITS). DISTANCE BETWEEN ELECTRODES 0.52 MM  
PRIMARY CURRENT 1.5 AMP (FROM COWARD AND METER)

|   |       |       |                   |       |      |
|---|-------|-------|-------------------|-------|------|
| Methane in mixture, %.....                        | 3.12  | 6.22  | 8.49              | 11.18 | 100  |
| Converted volume per spark, mm <sup>3</sup> ..... | 0.55  | 0.77  | 0.59 <sup>1</sup> | 0.22  | 0.14 |
| Methane consumed per spark, mm <sup>3</sup> ..... | 0.017 | 0.048 | 0.050             | 0.025 | 0.14 |

<sup>1</sup> Current intensity 1.40 amp (cf. text).

sandths of a second, *e.g.*, at 1.50 amp there were 35 to 40 oscillations during 0.0023 sec; at 2.75 amp a countless number of oscillations during 0.0081 sec.

If, instead of inductor sparks, condenser sparks were used—duration less than 0.00003 sec—with a voltage just under the ignition point, a volume per spark of about 0.90 mm<sup>3</sup> of an 8.47 per cent mixture of methane and air was consumed, noticeably more (around 0.5 mm<sup>3</sup>) than in inductor sparks, but of the same order of magnitude.

Coward and Meiter compare their results with those of Morgan<sup>1</sup> on the bases of a simplified theory of heat. From a pointlike, momentary source of heat which produces the quantity of heat  $Q$ , the heat spreads in such a way that the distribution of temperature<sup>2</sup> is given by

$$T - T_0 = \frac{Qe^{-r^2/4\kappa t}}{8\bar{c}(\pi\kappa t)^{3/2}}$$

in which  $T$  is the temperature,  $T_0$  the temperature of the surroundings,  $\bar{c}$  the mean heat capacity of the gas per cm<sup>3</sup>,  $\kappa$  the temperature conductivity,  $t$  the time, and  $r$  the distance from the pointlike source of heat (see Fig. 39).

If a certain point is selected, with  $r > 0$ , the temperature rises at first, then drops again. The farther this point is from the source of heat, the lower is the maximum temperature reached. With the aid of the equations given above, one can readily compute how great a volume has been heated up to, or above, a certain given temperature and within what time. In the experiments of Morgan, a condenser spark with a gap of 1.0 mm and just capable of igniting an 8.8 per cent methane and air mixture had an energy of 0.0009 cal. For this energy and a point-shaped source, Coward and Meiter compute the volumes given in Table 11, which are heated to a definite temperature in a definite time.

These volumes ought to be comparable with the volume of 0.9 mm<sup>3</sup> which was converted in Coward and Meiter's experiments with condenser discharges that were just under those required for ignition.

For methane, ignition temperatures of 700°C were given. Coward and Meiter point out correctly, however, that at these temperatures induction periods of some seconds elapse before ignition. At 800°C,

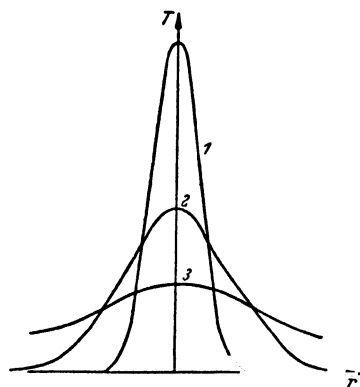


FIG. 39.—Temperature distribution in the neighborhood of an instantaneous, pointlike source of heat for various intervals.

<sup>1</sup> MORGAN, J.D., *Phil. Mag.*, **45**, 968 (1923).

<sup>2</sup> Cf. Frank-Mises, cited on p. 49.

the induction period is less than 1 sec, and it is justifiable to give an ignition temperature in which the induction period is of the same order

TABLE 11.—GAS VOLUMES THAT REACH A DEFINITE TEMPERATURE WITHIN THE TIME  $t$ ; THE SOURCE OF HEAT IS AN INSTANTANEOUS SUPPLY OF 0.0009 CAL AT A POINT (FROM COWARD AND MEITER)

| Temperature,<br>°C | Volume,<br>mm <sup>3</sup> | Time<br>$t$ , sec   |
|--------------------|----------------------------|---------------------|
| 700                | 1.24                       | $3.4 \cdot 10^{-3}$ |
| 1000               | 0.87                       | $2.7 \cdot 10^{-3}$ |
| 1200               | 0.72                       | $2.4 \cdot 10^{-3}$ |
| 1500               | 0.58                       | $2.0 \cdot 10^{-3}$ |

of magnitude as the periods appearing in Table. 11. That could be the case in a temperature lying several hundred degrees above the lowest ignition temperature. At any rate, one then arrives at the result that the gas volume consumed in a spark (in Coward and Meiter's experiments) is of the same order of magnitude as the volume heated by a spark (in Morgan's experiments) to an ignition temperature suitable for sufficiently short induction periods.

Even though these considerations show that we can arrive at satisfactory results on the basis of a simplified theory of heat, we shall nevertheless see (especially from the experiments of Finch and associates; cf. Chap. X) that these concepts alone do not suffice. We wish to emphasize, however, that with a theory not purely thermal in character, diffusion, perhaps especially that of free atoms and radicals, comes into play. Since diffusion follows the same laws as those for heat conduction, it is completely conceivable that concepts of a purely thermal theory can be retained. Applied with the proper caution, it is likely that, in spite of all these limitations, the view of the theory of heat can occasionally perform a useful service.

## CHAPTER III

### PROPAGATION OF EXPLOSIONS

**1. General Remarks.**—Our interest in this chapter is directed to the propagation of an explosion when started at one point of an explosive mixture by means, for example, of an electric spark, a hot surface, a flame, or similar means. It is generally known that an explosion can be caused in a large volume of gas from some one point. We want to know principally with what velocity the explosion proceeds. We shall see first of all that two factors unite to determine the velocity. One is the more or less accidental factor of the gas flow depending on prevailing external conditions, and the other is an entity characteristic of the explosive mixture—an entity that remains for the velocity of flame propagation after all influences on the flow have been eliminated, namely, the “normal velocity of combustion.” This latter entity is the more interesting from the standpoint of physical chemistry. An attempt will therefore be made to dissociate it from the more complicated results and to bring it in relation to the entities of reaction velocity, heat conductivity, etc. The entity of the normal velocity of combustion is also a determining factor when a gas burner fed with a suitable mixture “pops” (*e.g.* a Bunsen burner fed with illuminating gas and air). A knowledge of this factor is therefore of importance in all cases in which burners with premixed gases are used for technical purposes. The best method for determining the velocity of reaction makes use of the Bunsen burner (*cf.* page 84).

Even though the velocity with which flames propagate in a variety of containers (open and closed tubes, bombs, etc.) is much more complicated than the normal velocity of combustion because of the result of flow influences, it must nevertheless be kept in mind that, especially in technical applications (*e.g.*, in the internal-combustion engine), we are often dealing with a progressive explosion, in contrast to the static explosion of the Bunsen burner, and that therefore the study of progressive flames is at least as important technically as that of static flames. In the explosion of firedamps and in similar explosions occurring in industrial plants, we are dealing with flames propagating themselves from some one point. The study of these processes for the purpose of preventing such explosions necessitates an acquaintance with flame propagation. It therefore follows that we first attempt to determine the less complex entity of the normal velocity of combustion and treat

the corresponding methods in greater details. But we shall also go beyond all this and take up the circumstances surrounding propagating flames, the methods for measuring their speed and the laws connected with these phenomena.

By flame we commonly mean a rapid chemical change occurring in a *thin* layer, accompanied by luminosity.<sup>1</sup> It is practical to differentiate two kinds of flames. An example of one type is the candle flame. Fuel vapor rises from the wick and can burn in the neighborhood of the wick only to the extent that it is mixed with oxygen from the air, be it by diffusion or by turbulence. For this type of flame, it is therefore characteristic that the combustion process and the mixing process are combined and that the mixing process can sometimes even become the important factor. In such cases, we speak of diffusion flames. In the firing done on a large scale in industry, however, where nonpremixed gases are used, turbulence and not diffusion can be the determining factor. This type of flame will be discussed in Chap. VI. In the turbulent category also belongs the case of combustion in the outer ring of an ordinary Bunsen burner.

In flames of premixed gases, on the other hand, we are dealing with something different. Here we have an explosive mixture at the very outset. The flame is the luminous zone (called the "surface" for the sake of simplicity), in which fresh gas and burned mixture meet and which pushes forward to the fresh gas. That the flame is luminous is fundamentally of secondary importance. Actually, however, probably all flames in explosive mixtures are luminous. A part of the luminosity comes not from the combustion zone itself but from the afterglow of the burned gases behind the combustion surface. In premixed explosive gases, the flame is therefore identical with the explosion zone.

In observing and measuring the flame speed, one almost always makes use of luminosity. There are, however, methods independent of it. It is possible, for example, to deduce the flame speed from the rise in pressure in bombs (*cf.* page 144). One can also devise methods for measuring the speed by the ionization of the flame gases. For example, electrodes are attached at suitable distances as electrical probes in which a current flows only when the gas between them is reached by the flame and so ionized. If the time at which a short circuit appears at the various probes is registered, the speed of flame propagation can be computed. This method has the advantage of being adaptable in combustion chambers that are difficult of access, *e.g.*, the inside of a motor in operation.<sup>2</sup>

Here we shall point out that, for the normal velocity of combustion,

<sup>1</sup> Luminosity is not essential, but it is almost always present. *Cf.* ELLIS, O.C. DE C., and W.A. KIRKBY, "Flame," Methuen, London, 1936.

<sup>2</sup> *Cf.*, *e.g.*, SCHNAUFER, B.K., *Z. Ver. deut. Ing.*, **75**, 455 (1931).



values from several decimeters up to several meters are generally found. Flame speeds can be of similar order of magnitude, but they can also assume values of up to several hundred meters per second. Finally, flames can in extreme cases change over into a "detonation," *i.e.*, a particularly rapid combustion with velocities of 1 to 4 km/sec. The characteristic feature of a detonation is the fact that a percussion wave (*cf.* pages 160*ff.*) that propagates at a high velocity (greater than sound) is connected with the zone of chemical conversion. Detonation is basically a simpler process than ordinary combustion. Its velocity is quite independent of external disturbances, if only because the velocity of detonation is much greater than the velocity of any process coming into consideration as a disturbance. It can be computed by means of the general equations for hydrodynamics and thermodynamics without the necessity of reaction-kinetic data. These processes will be treated separately in Chap. V.

It is further of interest to gain an insight into the mechanism underlying flame propagation. We shall see that the normal velocity of combustion is caused by the joint effect of heat conduction (transference of thermal energy from the burned gases to the fresh gas) and diffusion (specifically diffusion of fresh gas molecules into the hot combustion zone and, under certain circumstances, diffusion of active particles from the combustion zone into the fresh gas). It is also caused, of course, by diffusion of the chemical reaction, on the velocity of which the speed of the flame in large part depends. With a knowledge of the mechanism, it is possible to see how far the normal velocity of combustion can be increased or diminished by the addition of other elements.

The position of the ignition limits is directly connected with the magnitude of the combustion velocity, for a mixture that no longer shows a finite velocity of flame propagation can obviously no longer ignite. The ignition limit is here understood to be a function of the composition of the mixture (and possibly of the temperature and pressure), in other words, the limits in the composition below and above which no self-propagating explosion can be caused by external manipulation. The location of these limits generally depends on experimental factors and the source of ignition (spark, etc.). The limit beyond which no ignition can be expected for lack of fuel is called the "lower limit of explosion," and the limit toward an excess of fuel is called the "upper limit of explosion" (*e.g.*, in the case of hydrogen in air under the usual conditions, the lower limit of explosion lies at about 5 to 9 per cent, the upper at about 70 per cent hydrogen). The limits of explosion in this sense, as limits of composition outside of which no explosion can be caused by external ignition, must be distinguished from the pressure limits for auto-ignition (*cf.* Chap. I, page 13). To avoid misunder-

standing, we shall speak of ignition limits for spark ignition and the like, and of explosion limits for auto-ignition.

**2. Normal Velocity of Combustion.**—An explosion introduced into a sufficiently large section<sup>1</sup> of an explosive mixture propagates in the unburned mixture at a definite velocity. One must distinguish between a gross velocity with which the ignition of a gas in a tube, or the like, takes place as compared to the explosion, and the normal combustion velocity, or the velocity with which the border surface between burned and unburned gases moves, relative to unburned gas at rest in immediate proximity to the combustion surface. If a gas mass is ignited within itself, the expansion of the burning gas results in a considerable additional displacement of the burning surface.

Concerning the terminology, it should be pointed out that in the technical literature the velocity of the movement of the explosion toward the unburned mixture is generally called "ignition velocity,"<sup>2</sup> but it seems more appropriate to apply this term to the movement of the explosion on the surface of solid fuels and explosives.<sup>3</sup> We shall therefore use the term "normal combustion velocity" or, for brevity, "combustion velocity." Misunderstandings will thus be avoided.

The question now arises of how the shifting of the burning surface relative to the unburned gas can be observed directly, or how this entity can be measured indirectly.

In order to fix once more the concept of the normal velocity of combustion, let us consider Fig. 40. There the shaded portion represents the mixture already burned at the time  $t$ , which is to be separated by the burning surface  $F^*$  from the fresh gas to the right. In a volume element of fresh gas bordering on the burning surface at a point  $P$ , we imagine a system of coordinates in the fresh gas, the  $x$ -axis of which coincides, let us say, with the normal to the combustion surface in  $P$ . If the combustion surface  $F'$  intersects this normal in  $P'$  in a time  $t + \Delta t$ , then

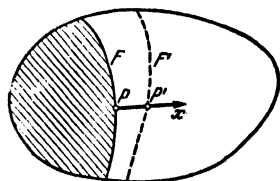


FIG. 40.—Definition of the "normal combustion velocity"; compare the text.

$$v_n = \lim \frac{PP'}{\Delta t} = \frac{dx}{dt} \quad (1)$$

<sup>1</sup> As can be seen from what was said in Chap. II, pp. 49ff., on spark ignition, an explosion introduced into a very small section need not always propagate.

<sup>2</sup> The term "ignition velocity" is likely to cause misunderstanding, because it seems to suggest that the actual combustion follows ignition after some period of time.

<sup>3</sup> Cf. MACHE, H., "Die Physik der Verbrennungerscheinungen," Leipzig, 1918.

\* "Burning surface" is for the time being, of course, only a fiction. As we shall see later, a continuous transition from fresh gas to burned gas takes place. The transition takes place in so thin a layer, however, that, for many considerations, like

is the normal combustion velocity. Under arbitrary experimental conditions, a system of reference connected with the fresh gas in front of the burning surface will generally be lacking, and it will therefore be difficult to determine  $v_n$ .

If it were possible to give the burning surface the exact form of a plane, one could imagine the normal combustion velocity as determined in the following manner (Fig. 41). Let the combustion surface  $F$  be perpendicular to the axis of a cylindrical tube. Let fresh gas flow from the right with a uniform velocity so regulated that the combustion surface remains stationary. Then the flow velocity of the fresh gas is just equal to the normal combustion velocity  $v_n$ . This is the method

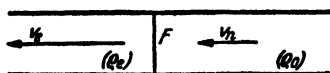


FIG. 41.—Flow velocity  $v_n$  (normal combustion velocity) of the fresh gas and  $v_e$  of the terminal gases in a cylindrical tube with a static, even-burning surface  $F$  (experimentally not realizable).

that Bunsen<sup>1</sup> has described in principle for determining this entity. Disregarding the influence of the tube wall, which makes ideal conditions in the combustion zone impossible—a thing it is customary to point out—general hydrodynamic considerations make it impossible to realize flow conditions in which the burning surface is exactly plane (*cf.* page 93). As a quantitative method for determining  $v_n$ , this procedure is therefore not suitable. Nevertheless, the velocity thus computed has a certain practical value. For a given tube diameter ( $v$  determined in this manner will not be independent of the tube diameter), the  $v$  thus determined will be the exact velocity below which the gas flow cannot fall if the burner is not to “pop.” In a corresponding form, this method was also described by Bunsen.

Figure 41 discloses another relation. Let the fresh gas flowing from the right with the velocity  $v_n$  have the density  $\rho_0$  and the temperature  $T_0$  (abs). The burned gases are to have the temperature  $T_e$  and the density  $\rho_e$ . They are to flow with the velocity  $v_e$ . Because of the hydrodynamic continuity requirement (in a stationary condition, the same gas mass must flow per unit of time through every cross section of the tube), the following is valid:

$$v_n \rho_0 = v_e \rho_e \quad v_e = v_n \frac{\rho_0}{\rho_e} \quad (2)$$

and, if the reaction takes place without change in the mol-number,

$$\frac{\rho_0}{\rho_e} = \frac{T_e}{T_0}$$

the above, for example, the introduction of the concept “burning surface,” in which density, composition, and temperature constantly change, is very convenient.

<sup>1</sup> BUNSEN, R., *Poggendorffs Ann.*, **131**, 161 (1866).

Since the density of the hot combustion gases is considerably smaller than that of the cold fresh gas,  $v_e$  will generally be several times greater than  $v_0$ ; i.e., the burning surface is a surface in which not only gas density, composition, and temperature, but also the gas velocity,<sup>1</sup> change erratically. If, as the result of reaction, the temperature rises from 300° to 2400° abs—assuming that the change of the mol-number in the conversion can be ignored— $v_e$  will be eight times  $v_0$ . Relative to the fresh gas, the exhaust gases move with a velocity of (Fig. 42)

$$v_r = v_e - v_n = v_n \left( \frac{\rho_0}{\rho_e} - 1 \right) \quad (3)$$

Geometrically, the situation is simplest if a large volume enclosed in a spherical container is ignited in the center. Since, in the case of a solid container, the pressure must rise and the progress of the explosion is complicated by the compression of the fresh gas by means of combustion

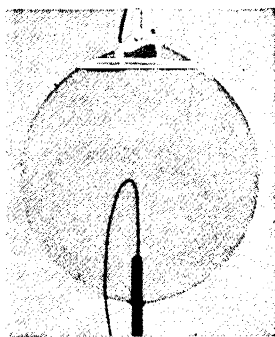


FIG. 43.—Soap bubble for determining the normal combustion velocity. [From Fiock and Marvin, *Chem. Rev.*, vol. 21 (1937).]

gases (cf. pages 138ff.), we shall here consider only the simplest case of a “bomb of constant pressure” but of variable volume, which can be experimentally realized and has actually been realized for purposes of measurement<sup>2</sup> by enclosing the explosive mixture in a soap bubble (Fig. 43) and igniting it in the center by a spark. The progress of the flame is most conveniently registered photographically by means of a rotating drum (Fig. 44a).<sup>3</sup> A slit permits the equator of the bubble to be measured. The result is the flame pictured in Fig. 44b. With ignition at  $O$ , the flame has spread from the point of ignition to both sides. Since the film was simultaneously moved upward at a known rate of speed, we get the

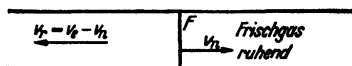
result pictured in Fig. 44b. Given the scale of the figure, the velocity of the flame is calculated from the slope of lines  $OM$  and  $ON$ , respectively. This, however, is only the actual velocity of the flame; to compute the normal combustion velocity, (2) must be applied

$$v_n = v_e \frac{\rho_e}{\rho_0}$$

<sup>1</sup> And with it the pressure (cf. p. 80), but in ordinary flames by only very small amounts.

<sup>2</sup> STEVENS, F.W., *NACA Repts.*, **305** (1929); **372** (1930).

<sup>3</sup> As Mallard and Le Chatelier first measured flames in tubes; cf. p. 92.



(Frischgas ruhend = fresh gas static)

FIG. 42.—Ideal case, progress of an even-burning surface  $F$  with the velocity  $v_n$  toward the static fresh gas.

$\rho_e$  and  $\rho_0$  are in inverse relation to the corresponding volumes, and the latter according to the third power of the radii of the sphere

$$\frac{\rho_e}{\rho_0} = \frac{r_0^3}{r_e^3} \quad (4)$$

$r_0$ , the radius of the original bubble, can be measured directly;  $r_e$  can be computed from Fig. 44*b*, given the scale, since the distance  $MN$  corresponds to the diameter of the sphere. It is therefore possible to compute  $v_n$  directly.

This method has been applied practically in only a very few cases, but it seems to be quite reliable and can be recommended, since it

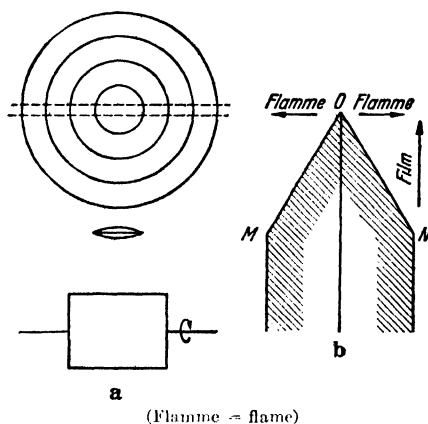


FIG. 44.—Recording the flame spread in a soap bubble on a rotating drum.

appears to have only few uncontrollable sources of error (for results, see page 70).

Instead of the photographic registration of Fig. 44, a series of snapshots at brief intervals can be made if a camera with suitable stops is available. Results like those of Fig. 45 are then obtained, and the flame velocity can be computed from them.

The soap-bubble method of Stevens<sup>1</sup> has been discussed in detail by Fiock and Marvin.<sup>2</sup> Stevens originally obtained values for the normal velocity of combustion of CO-O<sub>2</sub> mixtures which could be very well represented by the mass-action relation<sup>3</sup>

$$v_n = k[\text{CO}]^2[\text{O}_2] \quad (5)$$

<sup>1</sup> STEVENS, F.W., *NACA Tech. Repts.*, 176, 280, 305, 337, 372, 1923; *J. Am. Chem. Soc.*, **48**, 1896 (1926); **50**, 3244 (1928); *Ind. Eng. Chem.*, **20**, 1018 (1928); *Sci. Monthly*, **32**, 556 (1928).

<sup>2</sup> FIOCK, E.F., and C.F. MARVIN, *Chem. Rev.*, **21**, 367 (1937).

<sup>3</sup> Cf. also Chap. VIII.

a relation that was hardly intelligible theoretically because—even granted that a reaction velocity given by the simple expression (5) were determining for  $v_n$ —the decisive temperatures and therefore  $k$  would necessarily be different for different mixtures. In fact, Eq. (5) is not confirmed by recent observations (Fiock and Marvin). Since the gases always absorb water vapor from the bubble, exact work is possible only if one uses a known  $H_2O$ -vapor pressure. For that reason, Fiock and Marvin in all their experiments work with a vapor content of the gases of 2.69 per cent (on the influence of water vapor on the combustion velocity of carbon monoxide, see page 121). The values obtained for 25°C are graphed in Fig. 46, where  $v_e$  is the measured flame velocity,  $E(=r^3/r_0^3)$  is the expansion relation, and  $v_n = v_e/E$  is the normal velocity of combustion computed from both. The normal velocity of combustion, as in most cases (*cf.* page 71), shows its maximum, not with the stoichiometric mixture, but rather with a slight excess of fuel. There are systematic variations between  $v_n$  and the expression  $k[CO]^2[O_2]$ , but even so the expression above is a fairly good approximation over a certain range.

By the same method, the flame velocity of  $CO-O_2$  mixtures with various additions of inert gas (He and A) were investigated. Independent of special considerations, a decrease of the flame velocity is theoretically to be expected when foreign gases are added (*cf.* page 112; not, however, in detonation; *cf.* Chap. V). Experiments support this view. Argon decreases the velocity more than helium. We shall discuss probable sources of error in this method below.

The photographs in Fig. 45 by Fiock and Marvin can serve to prove that the spread of the flame in the "constant-pressure bomb" actually proceeds in concentric spheres. Similar photographs by Khitrin<sup>1</sup> are available.

The Bunsen method mentioned above is, to be sure, not suitable

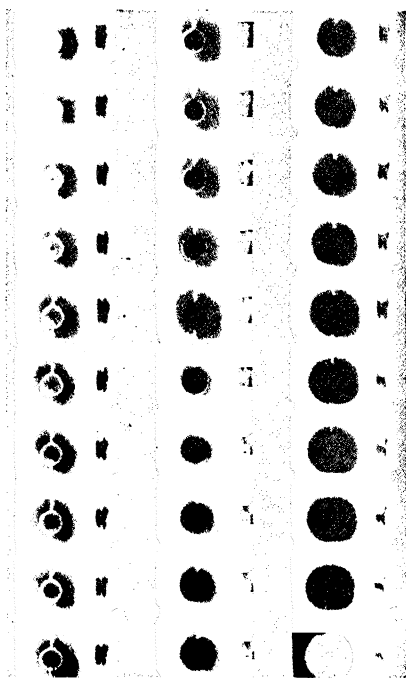


FIG. 45.—Photographs of an exploding soap bubble (1610 frames/sec). (From Fiock and Marvin.)

<sup>1</sup> KHITRIN, L., *Tech. Phys. USSR*, **3**, 1028 (1936).

for quantitative measurements, but one can, like Bunsen, proceed from this method of presenting the problem.

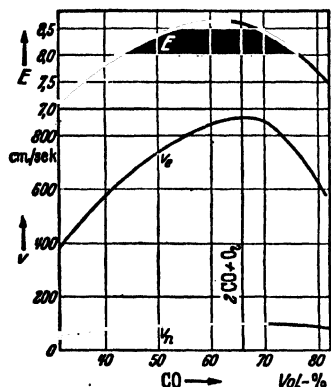


FIG. 46.—Measurements according to the soap-bubble method by Fiock and Marvin (p. 67) made on carbon monoxide and oxygen mixtures. Flame velocity  $v_n$ , expansion ratio  $E$ , and normal combustion velocity  $v_n$ .

The normal velocity of combustion is to be determined by making the combustion surface static by counterflow of the fresh gas. However, the form of the combustion surface must not be prescribed at the outset. One will then be pretty well forced to study the conditions prevailing in the Bunsen burner. These conditions (Fig. 47), as is well known, can be put thus: The fresh gas mixture flowing from below burns in the inside cone<sup>1</sup> of the burner. This cone burns with a bluish or greenish flame depending on the composition of the mixture; and, according to work done by Haber,<sup>2</sup> the mixture in the inner cone is so completely burned to  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$  in the conversion process that these materials appear in concentrations that corre-

spond to the water-gas equilibrium occurring at the temperatures reached. This water gas, which could not react as such, mixes with fresh air in the outer cone of the burner by diffusion, and partly perhaps also by whirling and turbulence, and reacts with continued weak luminosity to form  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

At any rate the mantle surface of the inner cone is to be considered as the stationary but not the plane burning surface of the fresh gas, *i.e.*, as the zone of a stationary explosion. A more detailed analysis of the relations that connect the form and size of the inner cone with the rate of flow of the fresh gas and the normal velocity of combustion goes back to Gouy,<sup>3</sup> whose work was continued by Michelson.<sup>4</sup> The most reliable discussion of the phenomena, taking into account what had appeared until 1917, can be found in Mache.<sup>5</sup>

If one assumes with Gouy a constant normal velocity of combustion [an assumption that will not be realized for the immediate proximity of the wall because of conduction, as well as in



FIG. 47.—Sketch of the Bunsen burner.

<sup>1</sup> We shall use here and elsewhere the common term "cone," although it is really not a cone but more a general surface of revolution.

<sup>2</sup> HABER, F., and F. RICHARDT, *Z. anorg. Chem.*, **38**, 1 (1903).

<sup>3</sup> GOUY, *Ann. chim. phys.*, **18**, 27 (1879).

<sup>4</sup> MICHELSON, *Wiedemanns Ann.* **37**, (1889) 1; for further quotations, cf. Mache.

<sup>5</sup> MACHE, H., "Die Physik der Verbrennungserscheinungen," Leipzig, 1918.

areas with a sharp bend of the combustion surface (cone tip of the Bunsen burner)], the following picture results (Fig. 48). If one designates the cross section of the mouth of the burner as  $F_0$  and the average rate of flow of the fresh gas as  $v_f$ , then, to prevent the burner from popping,  $v_n \leq \bar{v}_f$ . On the other hand, all the fresh gas flowing in a unit of time, namely,  $F_0 \bar{v}_f$ , must be converted in the burning surface with a magnitude designated by  $F$ . The quantity converted in the unit of time is equal to the burning surface times the normal velocity of combustion, and the following equation therefore applies.

$$F_0 \bar{v}_f = F v_n \quad v_n = \bar{v}_f \frac{F_0}{F} \quad (6)$$

If one assumes the burning surface to be a cone with the angle  $\vartheta$ , and if  $r_0$  is the radius of the mouth of the burner, then

$$F_0 = \pi r_0^2 \quad F = \frac{\pi r_0^2}{\sin \vartheta}$$

and therefore

$$v_n = \bar{v}_f \sin \vartheta \quad (7)$$

All the results that follow, go back to this simple formulation. For that reason, it is not necessary to introduce the precise assumption of a cone-shaped surface of combustion; rather, one can resort to Eq. (6), which is completely exact as far as one can assume a constant normal combustion velocity.

We shall now consider the relations at the surface of combustion in detail. Through the element of  $d$ , perpendicular to the direction of flow of the fresh gas  $v_f$ , in a unit of time, the quantity of gas flowing is (Figs. 48 and 49)  $d v_f$ . Let  $F$  again be the combustion surface pictured in the illustration. The flow tube with the cross section  $d_0$  cuts out of this surface an element

$$d\omega = \frac{d_0}{\sin \vartheta}$$

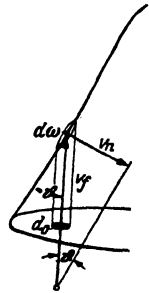


FIG. 49.

and, since combustion is to proceed normally in respect to this element, the quantity burned in the unit of time is

$$d\omega v_n = d_0 \cdot \frac{v_n}{\sin \vartheta}$$

since the converted quantity must be equal to that flowing in, namely,  $d_0 v_f$ , it follows that

$$d_0 \frac{v_n}{\sin \vartheta} = d_0 v_f \quad (8)$$

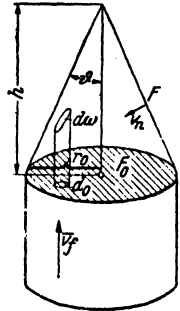


FIG. 48.—Theory of the Bunsen burner.



or

$$v_n = v_f \sin \vartheta \quad (9)$$

If the rate of flow were constant over the entire cross section of the tube, parallel to the axis of the tube, and equal to  $\bar{v}_f$ , the equation above would be valid for every point; and, insofar as one demands that the burning surface rest on the edge of the burner, one would get a straight circular cone (Fig. 48) and thus the relation of Eq. (7). The greater the velocity of the fresh gas, the more pointed the cone; the greater the combustion velocity, the blunter the cone.

If  $\bar{v}_f$  is measured and if the angle is computed [or what is equivalent, the height of the cone  $h$  when the radius of the burner is known (Fig. 48)],  $v_n$  can be computed by means of (7) without difficulty. This method was first used by Michelson and then expanded at the Gas Institute of Karlsruhe by Bunte, Ubbelohde, and associates. Aside from obvious advantages of the method, it is clear that it will be especially suitable for all cases involving the use of gas in burners.

We shall give some of the results obtained by this method and then add a few remarks of a systematic nature. A survey of some of the combustion velocities of fuel mixtures with air obtained by this method is presented in Fig. 50.<sup>1</sup> The smallest measurable normal combustion velocities (in the neighborhood of the ignition limits) are about 20 cm/sec; the maximum value for hydrogen in air is around 267 cm/sec; the maximum velocity of hydrogen-oxygen mixtures is about 9 m/sec. A systematic discussion of the velocities obtained and the influence upon them by external factors like temperature and pressure, as well as the treatment of their dependence on the composition of the mixtures and on addition of inert gases, will be added later in the proper connection (pages 88, 89, 121). Since the dynamic method by Gouy as well as Stevens's soap bubble method are directed toward the measurement of undisturbed normal combustion velocity, the numerical values obtained by both methods should coincide. Unfortunately little material that can be compared exists as yet, and therefore no conclusions on the variations in the values obtained by both methods are as yet justified.

<sup>1</sup> Cf., in this connection, UBBELOHDE, L., and O. DOMMER, *Gas- u. Wasserfach*, **57**, 733, 757, 781, 805 (1914). UBBELOHDE, L., and E. KOELLIKER, *Gas- u. Wasserfach*, **59**, 49 (1916). BUNTE, K., and LITTELSCHIEDT, *Gas- u. Wasserfach*, **73**, 837, 871, 890 (1930). BRUCKNER, H., and G. JAHN, *Gas- u. Wasserfach*, **74**, 1012 (1931). BUNTE, K., *Gas- u. Wasserfach*, **75**, 213 (1932). PASSAUER, *Gas- u. Wasserfach*, **73**, 313, 343, 369, 392 (1930). JAHN, G., and G. MÜLLER, *Gas- u. Wasserfach*, **76**, 756 (1933). BUNTE, K., and G. JAHN, *Gas- u. Wasserfach*, **76**, 89 (1933). UBBELOHDE, L., and M. HOFÄSS, *Gas- u. Wasserfach*, **56**, 1225 (1913). UBBELOHDE, L., and R. ANWANDTER, *Gas- u. Wasserfach*, **60**, 225 (1917). Cf. also the Karlsruhe dissertation by E. Hartmann, 1931 (from which the illustration above is taken). Likewise see G. Jahn, 1934.

The example of  $\text{CO-O}_2$  is not especially well suited for purposes of comparison because of the great dependence of the normal combustion velocity on water-vapor concentration. In support, it might be pointed out that Jahn<sup>1</sup> found a maximum combustion velocity of 107 cm/sec for carbon monoxide which contained 1.5 per cent  $\text{H}_2$  and 1.35 per cent  $\text{H}_2\text{O}$  in mixture with oxygen (adulterated with 1.5 per cent  $\text{N}_2$ ). Jahn applied the dynamic method, and his results coincide satisfactorily with

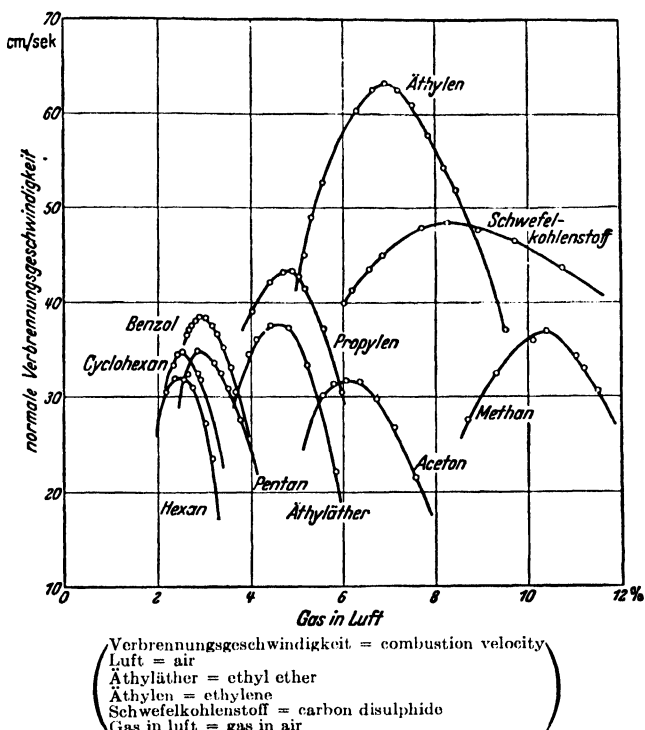


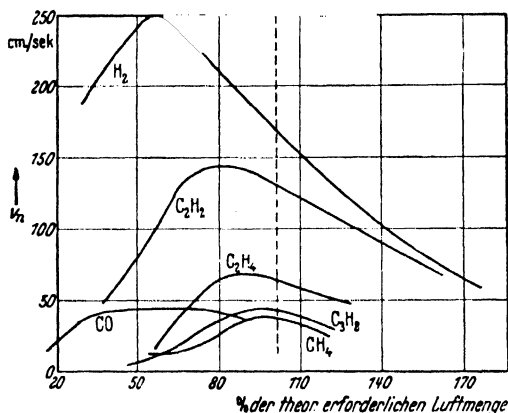
Fig. 50.—Normal combustion velocity of various materials in mixture with air. [From Hartmann, Karlsruhe Dissertation (1931).]

Fiock and Marvin's value of about 100 cm/sec for  $\text{CO-O}_2$  mixtures with 2.65 per cent  $\text{H}_2\text{O}$  (quoted page 69). The mixture of maximum combustion velocity has a content of 77.5 per cent  $\text{CO}$  in Jahn's experiments. In other words, it also tends toward the side of highest fuel content and away from the stoichiometric mixture.

A better survey of the normal combustion velocities depending on fuel concentration can be obtained, if one does not plot the content of fuel by percentages in the usual manner but instead chooses as the

<sup>1</sup> Cf. also the Karlsruhe dissertation by E. Hartmann, 1931 (from which Fig. 50 was taken). See also G. Jahn, 1934.

abscissa the content of primary air (or oxygen) in percentages of that required for complete combustion (Fig. 51). This presentation corresponds to that usually chosen in engine combustion with the excess air number  $\lambda$ . We present in this connection some of the results by Smith.<sup>1</sup> Figure 51 shows clearly that the mixtures of maximum combustion velocity always lie in the direction of excess fuel.



(% der theor. erforderlichen Luftmenge = per cent of the quantity of air theoretically required)  
 FIG. 51.—Normal combustion velocities of various materials in mixture with air. (From F.A. Smith, *Chem. Rev.*, vol. 21 (1937).]

**3. Extended Theory of the Bunsen Flame.**—The discussion regarding the formulation of the principles of the Bunsen burner is based on two assumptions, both of which obviously cannot be realized.

1. That the flow be constant for the entire cross section.
2. That the flow into the free gas space be continued in the same manner as in the tube of the burner, and especially that it should not be influenced by any reaction of the flame.

Obviously, there is no reason to regard these two assumptions as being self-evident; indeed, a logical and precise manner of deduction would demand that the hydrodynamic problem of the free-burning flame be treated in a rather general way, with statements of flow relations and the form of the combustion surface following in the nature of a solution. In this form, however, the problem has probably never been stated and certainly never solved.

We must content ourselves with pointing out existing difficulties and with discussing the matter as well as possible considering the experimental and theoretical data available.

So much is clear thus far: The assumption of a constant velocity of flow over the entire cross section will never be realized because of

<sup>1</sup> SMITH, F.A., *Chem. Rev.*, **21**, 389 (1937).

internal friction, and we can—as has actually been done in the literature without further discussion—give the distribution of velocity for the flow in the tube as laminar flow and deduce the form of the combustion cone; but presupposition 2 will still be needed. It is in any case useful to make clear what form of burning surface will result.

If we have laminar flow with adhesion of the gas to the wall (a fact generally supported by observation and assumed in the formulation of Poiseuille's law), a parabolic distribution of velocity over the cross section results with a value of 0 on the wall (Fig. 52). In this case, a different inclination of the burning surface toward the axis is involved for every value of  $r$ , the inclination obviously assuming a minimum at the axis itself. Without computing, it is clear that, for the burning surface, we obtain qualitatively the axis section  $F$ , as plotted in Fig. 52. But difficulties occur when  $r = 0$  (axis) and when  $r = r_0$  (the rim of the burner). For  $r = 0$ , the burning surface would have to have a sharp point, but this would run counter to all expectations and is moreover contradicted by direct observation. This difficulty is easily obviated (*cf.* page 76). Of fundamental importance, however, is what takes place on the rim. Since the velocity of the fresh gas  $v_f$  for  $r = r_0$  goes toward 0, there must be a value  $r_k < r_0$ , for which exactly  $(v_f)_{r=r_k} = v_n$ . For this value  $r_k$ , the burning surface, would have to be perpendicular to the axis, and for  $r > r_k$  there would be no static burning surface at all (Fig. 52). In the immediate proximity of the rim this is, to be sure, no longer the case, since, as we shall see below, the normal velocity of combustion will approach zero here as the result of heat conduction.<sup>1</sup>

At any rate, if we wish to overcome the difficulties presented by Fig. 52, it will be necessary to revise the assumptions on the condition of flow.

We can—although it does not correspond to assumptions usually made for flow—introduce a finite external gas friction on the wall of the burner. In this way, a finite gas velocity results there, and all difficulties are avoided. Although we are of the opinion that this assumption does not correspond to reality, we shall indicate in the following how Michelson, in a calculation reproduced by Mache, computed the form of the burning surface according to this method, because it seems to us the simplest relation enabling us to obtain a quantitative picture.

If we let the  $z$ -axis of a system of coordinates coincide with the axis

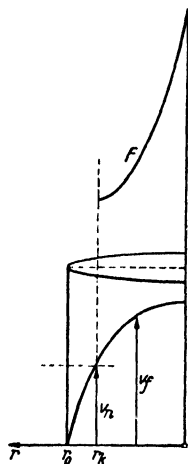


FIG. 52.—Flow velocity of the fresh gas,  $v_f$ , with laminar flow; the form of the burning surface,  $F$ , is derived.

<sup>1</sup> For further discussion on the form of the burning surface, *cf.* especially the works of L. Ubbelohde, quoted p. 72.

of the burner and add the  $r$ -axis perpendicular to it, we obtain with the former designations the following differential equation for the burning surface (Fig. 53):

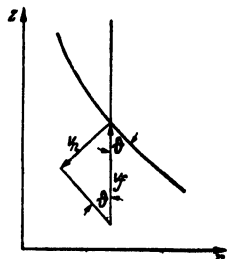


FIG. 53.

$$\frac{dz}{dr} = \cot \vartheta = \pm \frac{\sqrt{v_f^2 - v_n^2}}{v_n} \quad (10)$$

In this,  $v_n$  is again regarded as constant, whereas the function of  $r$  resulting from laminar flow with finite external friction (*i.e.*, slipping on the wall of the tube) is to be substituted for  $v_f$ . We then get

$$v_f(r) = \frac{\text{const}}{\eta} \left( r_0^2 - r^2 + \frac{2\eta}{\lambda} r \right) \quad (11)$$

in which again  $r_0$  is the radius of the burner,  $\eta$  the inner, and  $\lambda$  the external friction. If we place (11) in (10), we are finally led to elliptical integrals, the solving of which (given the numerical values for the constants) is simple with the aid of well-known tables. We refer the reader to Mache and will present only a special solution in graphic form (Fig. 54), according to Mache.

In the first place, the following is noteworthy: There are two solutions, a surface of revolution with its apex at  $C$  and one opposite it with its apex at  $D$ . In the second place, the sharp point of the burning surface is noteworthy. It now remains to show why only one of the two surfaces, the one with its apex at  $C$ , is observed. It is further necessary to show that this surface is really stable, *i.e.*, that it returns to its original position if it is displaced by small disturbances. As Mache has shown, this is possible only if a corollary assumption respecting the rim is introduced (we shall treat the condition at the rim of the burner later). If we assume that the burner is constantly ignited at the rim, we can see that only the upper cone, as we normally observe it, is stable; for, if we consider the lower cone and if we moved the point from  $D$  to  $D'$  by some external means, the velocity of flow of the gas would be the same, but the entire conversion would be decreased because of the decreased burning surface, and as a result the flame would have to be blown out of the tube. If, on the contrary, the apex were moved from  $D$  to  $D''$ , the combustion velocity would overbalance the flow components normal to the burning surface, and the burner would pop. At any rate, the lower cone would

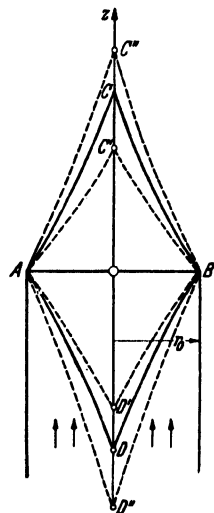


FIG. 54.—Computed burning surface,  $ACB$  or  $ADB$ . (From Mache, p. 69.)

thus be unstable. That the upper cone is stable in the face of such changes is obvious when one thinks of its tip displaced to  $C'$  or  $C''$ . In this case, the change of the size of the burning surface causes it to return to its original position.

That this, however, depends essentially on the assumption respecting the rim can be seen if we assume the point of ignition to be at  $D$  instead of on the rim. Then it is this point that is determined as the tip of the burning surface. By external means, only the position of the rim could be changed (Fig. 55) either to  $A'B'$  or  $A''B''$ . Analogous to the above situation, it can be seen that the burning surface will trend back to its original position, in other words, that with ignition at  $D$  the lower cone becomes stable.

In order to show that no sharp point but rather a rounded top forms at the upper end, it is necessary to make use of the theory of flame propagation. We therefore refer the reader to the discussion on page 127 and shall give here only the following. We have attempted to treat flame propagation as a purely thermal phenomenon, from the same point of view from which we treated the processes leading to ignition in the preceding chapters. The fresh gas is ignited to such an extent by heat conduction that by spontaneous reaction the temperature rises higher and higher by itself, etc. Accordingly, heat conductivity and reaction velocity dependent on the temperature are determining factors for the normal combustion velocity. This theory is incomplete for the same reasons that were discussed in the first chapter. The reaction velocity will not be a pure temperature function but will depend in large measure on chain-branching. Since free radicals or other active centers can continue the chain, the reaction into the unburned portion can be continued not only by heat conduction but also—and in special cases perhaps even predominantly—by the diffusion of active particles. Since the formal laws of diffusion coincide with those of heat conduction, the results that are important here would remain unchanged formally by the additional assumption of diffusion.

If combustion is propagated by heat conduction, the normal combustion velocity will increase with the heat flow, although perhaps not linearly with it, but presumably more since the reaction velocity is an exponential function of the temperature. If the burning surface has the form of a plane [more correctly, if the radius of curvature of the surface is very great compared with the "thickness of the burning zone" (estimation; see page 108)], then heating in front of the burning surface is given by

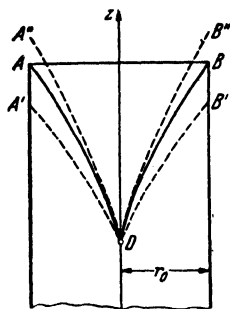


Fig. 55.

$$\frac{\partial T}{\partial t} = \kappa \frac{\partial^2 T}{\partial r^2} \quad (12)$$

if the  $r$ -axis runs in the direction of the normal of the burning plane, and  $\kappa$  is the temperature conductivity. If the burning surface is no longer a plane, however, the following is valid for heating, if we consider only the two borderline cases of a cylindrical or spherical burning surface—where the fresh gas is to be within the surface—both of which can be represented in dependence on only one radical, the radius  $r$ .

$$\frac{\partial T}{\partial t} = \kappa \left( \frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right) \quad (\text{cylinder}) \quad (13)$$

or

$$\frac{\partial T}{\partial t} = \kappa \left( \frac{\partial^2 T}{\partial r^2} + \frac{2}{r} \frac{\partial T}{\partial r} \right) \quad (\text{sphere}) \quad (14)$$

According to the computations by Mache and Michelson (*cf.* page 107),  $\partial T/\partial r$  becomes of the magnitude of  $50,000^\circ/\text{cm}$ ;  $\partial^2 T/\partial r^2$  can be estimated at an average of about  $2,500,000^\circ/\text{cm}^2$ . One can see that, in addition to the member (12) being solely determining in cases of planes, the second member (13) or (14) becomes noteworthy at small values of  $r$ , *i.e.*, small radii of curvature of the burning surface. With the above estimated values of  $\partial T/\partial r$  and  $\partial^2 T/\partial r^2$ , it can be seen that, even for  $r = 1$  mm, the second member in (13) or (14) is no longer negligible as compared with the first. All this means that the heating of the fresh gas is increased by a sharply curved burning surface. This fact suffices to explain qualitatively the action at the flame tip. As a result of the increased supply of heat, the normal combustion velocity has been increased to such an extent that the burning surface can remain static even normal to the direction of flow. A quantitative treatment would presuppose an exact theory of combustion velocity, which we do not yet have at our disposal.

It is much more difficult to understand the situation at the rim. We have pointed out on pages 75 and 76 that, in the case of laminar flow and infinite external friction—as it is assumed in formulating Poiseuille's law—the velocity of flow in the neighborhood of the rim must always become smaller than the normal combustion velocity, and that as a result the flame there would pop. Mache therefore assumed finite external friction in order to avoid this difficulty.

This difficulty, however, is not the only one affecting the rim phenomena. It is again Mache to whom we owe a discussion of the conditions prevailing here. He analyzes what takes place with one element of the burning zone (Fig. 56). The element at 0 would, as the result of flow of the fresh gas, move upward with a velocity of  $v_f$ . The normal

combustion velocity  $v_n = v_f \sin \vartheta$  takes care, to be sure, that the element cannot move out of the burning surface, but it does not prevent the element from moving within the burning surface with a velocity of (Figs. 53 and 56)  $v_t = v_f \cos \vartheta = v_n \cot \vartheta$ . The result would be, as shown in Fig. 57 from Mache, that an element of the burning surface

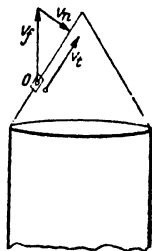


FIG. 56.—Tangential displacement,  $v_t$ , of an element of the burning surface. (From Mache.)

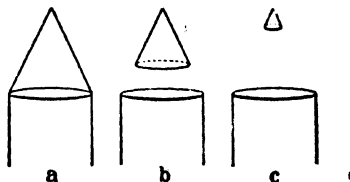


FIG. 57.—Extinguishing the burning cone from the rim; see the text. (From Mache.)

at the rim would move within the burning surface toward the point of the cone, and that the cone would be extinguished at the rim. As long as one holds to the view that the burning surface inclines toward the direction of flow, one cannot overcome this difficulty without a special corollary assumption. Mache points out that the flame at the rim must constantly be ignited anew, if it is not to be extinguished, and that it makes the mixing layer between the gas and the air function as the "ignition flame." Ubbelohde and Koelliker<sup>1</sup> point out that this explanation might not be adequate since a burning cone can also be static if the introduction of fresh air is made impossible, and thus a mixing layer cannot exist (e.g. in the use of a flame-splitting tube; cf. page 85).

It seems to us that the problem cannot be solved without a more exact consideration of the flow conditions. We shall therefore now discuss known facts about flow in the Bunsen burner.

If we keep to the view that the unburned gas moves axially and the burning surface lies diagonal to the direction of motion ( $\vartheta$ , Fig. 58), the direction of flow in the burning surface will change irregularly; thus the following equation is valid (with the same terms— $\rho_0$  and  $\rho_e$  are the densities,  $v_f$  and  $v_e$  the velocities of the fresh gas and the terminal gas).

$$\rho_0 v_f d\omega \sin \vartheta = \rho_e v_e d\omega \sin \varphi \quad (15)$$

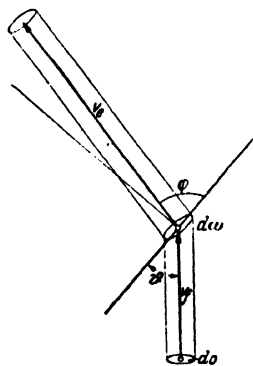


FIG. 58.—Breaking of the gas flow in the burning surface. (From Mache.)

<sup>1</sup> UBBELOHDE, L., and E. KOELLIKER, *Gas- u. Wasserfach*, **59**, 54 (1916).



because of the continuity of the gas flow; therefore

$$\frac{\rho_0 v_f}{\rho_e v_e} = \frac{\sin \varphi}{\sin \vartheta} \quad (16)$$

if the tangential component of the flow is to remain unchanged (since only an acceleration normal to the burning surface is caused by the combustion), then the following is valid:

$$v_f \cos \vartheta = v_e \cos \varphi \quad \frac{v_f}{v_e} = \frac{\cos \varphi}{\cos \vartheta} \quad (17)$$

and therefore

$$\frac{\rho_0}{\rho_e} = \frac{\tan \varphi}{\tan \vartheta} \quad (18)$$

Thus  $\varphi$  can be computed from the known data.

Direct experimental proof for this type of flow does not exist. To be sure, the flow of the burned gas can be made visible by the introduction of lycopodium seeds into the fresh gas which flash after contact with the burning surface (Mache, quoted page 70), but it might be difficult to decide with certainty whether the angle  $\varphi$  is  $90^\circ$  or, as Fig. 58 and Eq. (18) require, whether the angle is less than  $90^\circ$  by a finite but not very large amount. At any rate, observations on the flow of the fresh gas are lacking.

Corresponding to the sudden increase in gas velocity in the burning surface, there is a sudden increase in pressure. [This follows quite generally from hydrodynamic considerations such as those discussed in the treatment of detonation in Chap. V. The "Hugoniot-curve" shows in the branch to be ascribed to ordinary combustion that a certain (small) loss of pressure must correspond to the increase in volume in the transition from fresh gas to burned gas.] The conditions in respect to the Bunsen burner are discussed in greater detail by Mache.<sup>1</sup> He reports on the following experiment, for example: A mixture of illuminating gas and air consisting of 25 per cent of gas content (with  $v_a = 34.2$  cm/sec) flowed through a tube 1 cm in inside diameter with a velocity of 425 cm/sec. Before ignition, the pressure excess over the atmosphere amounted to 0.076; after ignition, it was 0.149 mm of water. The difference in pressure of 0.073 mm of water is therefore necessary to accelerate the gas in the burning surface to its terminal velocity; or, what is the same: in the acceleration caused by the volume expansion of the gases, the gases cause a recoil on the fresh gas, in which, as a result, the pressure rises by the amount of 0.073 mm of water.

For the assumption generally made implicitly or explicitly, that the gas movement in the free atmosphere is the same as in the tube of

<sup>1</sup> MACHE, H., "Die Physik der Verbrennungserscheinungen," pp. 44ff., Leipzig, 1918.

the Bunsen burner, Mache<sup>1</sup> cites a photograph made according to the schlieren method which shows a jet of gas (not ignited) coming from a Bunsen burner for a length of several decimeters with a gas velocity of about 3 m/sec. One can easily compute that on its way the jet of gas must have experienced considerable mixing by diffusion. At a distance of 30 cm from the mouth of the burner, *i.e.*, after  $10^{-1}$  sec contact with the air, the following mean square of displacement results:

$$\overline{\Delta x^2} = 2Dt \cong 5 \cdot 10^{-2} \text{ cm}^2 \quad (19)$$

if one assumes about 0.2 to 0.3 cm<sup>2</sup>/sec for the diffusion coefficient and puts  $t = 10^{-1}$ , or

$$\sqrt{\overline{\Delta x^2}} \cong 2.2 \cdot 10^{-1} \text{ cm} \quad (20)$$

That is, considerable mixing has taken place to an extent of over 2 mm from the boundary surface. We can therefore assume that the relatively sharp jet limit observable in Mache's photograph is to be regarded not as the limit of a real jet of gas but as the place of greatest drop in concentration ( $r'$ ) in the bell-shaped distribution curve of the concentration in a section perpendicular to the direction of the jet (Fig. 59). Insofar as turbulence prevails, the mixing can only be greater still.

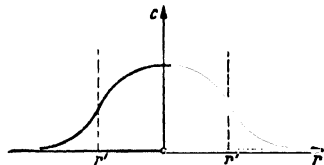


FIG. 59.—Combustion gas concentration  $c$  as a function of the distance between the axes  $r$  in a section perpendicular to the axis of the tube above the mouth of the burner.

As a further proof that a cohesive jet of gas emerges, it is stated that, if a wire ring is placed some distance from the mouth of a Bunsen burner and the gas above it is ignited, the cone of flame above this ring is formed the same as directly over the tube of the burner. It would still be necessary to show, however, that the burning cone over the wire is also quantitatively the same as the one ignited on the tube of the burner; otherwise, the study of the shape of the cone varying with the distance of the ring over the burner, as well as the study of the converted gas mass, would offer a method of arriving at statements on the actual state of the flow.

The gas flowing out of a tube under conditions as they exist for the Bunsen burner seems hardly to have been investigated in greater detail, either theoretically or experimentally. It is a matter in this case of the flow of a gas with friction in which the gas can be treated as practically incompressible.<sup>2</sup> As far as the condition of flow of the gas in the tube

<sup>1</sup> MACHE, H., "Die Physik der Verbrennungerscheinungen," pp. 44ff., Leipzig, 1918.

<sup>2</sup> The pressure differences appearing in the discharge are so small that the changes in volume caused by them may be ignored.

of the burner is concerned, it can clearly be considered either as laminar or as turbulent flow. As is well known, the Reynolds number is a criterion for this.

$$R_e = v \cdot \frac{l}{\nu} \quad (21)$$

in which  $v$  is the flow velocity,  $l$  the diameter, if a tube is used, and  $\nu$  the kinematic viscosity;  $\nu$  is given by

$$\nu = \frac{\eta}{\rho} \quad (22)$$

in which  $\eta$  is the viscosity and  $\rho$  the density. For air of room temperature,  $\nu$  amounts to about  $0.14 \text{ cm}^2/\text{sec}$ . The critical value of the Reynolds number, below which laminar flow is stable, lies at about 2000. It can be seen that, at a flow velocity of  $1 \text{ m/sec}$  and a tube diameter of  $0.5 \text{ cm}$ , the flow is certainly still in the laminar range, for then

$$R_e = 100 \cdot \frac{0.5}{0.14} = 360 \quad (23)$$

If the values of velocity and tube diameter are three times those given—and this still corresponds to possible conditions—the value of the Reynolds

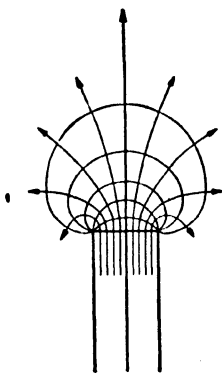


Fig. 60.

number is 3200, and the flow is fairly sure to be within the turbulent range. In the usual Bunsen burner (Teclu burner), the distance from the gas exit nozzle and the air intake to the mouth is so short (about  $10 \text{ cm}$ ) that, even though the value of the Reynolds number is below the critical value, it must be considered that in this short distance the flow has certainly not quieted down and is still turbulent. It seems, accordingly, that laminar flow is possible in experiments on the Bunsen burner, since a quietly and evenly burning cone has been achieved for observation by employing a sufficiently long and not too large a tube. However, in burners used in the laboratory or for technical purposes with a medium

or large diameter, it is necessary to deal with turbulent flow. Generally valid and simple equations are not therefore to be expected. Further, it is to be considered that, even if the flow in the tube is laminar, the condition in the proximity of the open end will vary considerably from that within the tube, and that the gas coming from the tube will not have the same distribution of velocity and direction as gas in the inside of a long tube.

If one had frictionless flow of such a kind that equal-velocity surfaces resulted, as in Fig. 60, the entire problem would be extremely simple. It would only be necessary to pick out the equal-velocity surfaces in

which the velocity of flow  $v$ , was equal to  $v_n$ . There the burning zone would be static. Such a solution is in principle excluded, however, because of flow with friction. Since in this case there is always a decrease in acceleration perpendicular to the direction of flow, one can never select a surface in which the velocity of flow is everywhere equal to  $v_n$  and in addition intersects normally to this surface directionally. For this reason, an attempt by Predvoditelev<sup>1</sup> to explain the form of the Bunsen burner by considering the burning surface a surface of selected velocity of the gas flow is unsatisfactory. He had found that, in gases that flow from wide openings (100 mm and above), a distribution of velocity forms in the free space which is approximately given by bell-shaped curves

$$v(z, r) \cong \frac{K}{z} e^{-\beta r^2}$$

in which  $z$  is measured in the direction of the tube axis with the zero point in the mouth, and  $r$  is the distance perpendicular from the axis. We realize, however, that this system of bell-shaped curves cannot be regarded as surfaces of equal potential flow, a thing that would contradict also the physical assumptions of the flow in question. If, on the other hand, the direction of flow is not perpendicular to these surfaces, the same considerations as above are needed to determine the static position of the burning surface. It is problematic in general simply to apply the results obtained from a large tube with probable turbulence to the narrow tubes of the Bunsen burner, where laminar flow prevails, at least in those experiments conducted to measure combustion velocities.

This much is correct, however, that it is necessary to know the conditions affecting flow in the free atmosphere around the burner before it is possible to proceed to an exact deduction of the form of the burning surface. Smith<sup>2</sup> gives preliminary results in this connection which were gained in the following manner: Light aluminum particles were mixed with an air current streaming out of the burner. From the path of these particles, the flow as well as the velocity of flow could be determined photographically. Measurements showed that, in a jet of gas coming out of a tube, a decrease in velocity took place in the middle of the tube [in distances of 1 to 2.5 burner diameters, the velocity decreased in the

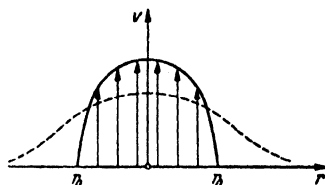


FIG. 61.—Condition of the flow as the gas leaves the mouth of the burner and enters the atmosphere; the solid line shows velocity distribution in the tube of the burner (radius  $r_0$ ); the broken line shows velocity distribution above the mouth of the burner.

<sup>1</sup> PREDVODITELEV, A., *Tech. Phys. USSR*, **2**, 364 (1935).

<sup>2</sup> SMITH, F.A., *Chem. Rev.*, **21**, 389 (1937).

neighborhood of the axis by about 3.4 cm/sec (per 1 cm of path)], whereas at the rim a rather large increase in velocity could be noted, as would be expected. The direction of flow remained essentially parallel to the axis of the tube. The effect of inner friction may therefore be presented as follows (Fig. 61): Let the solid curve represent the distribution of impulse in the mouth of the burner. As the jet progresses, a "diffusion"

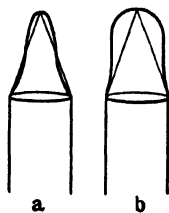


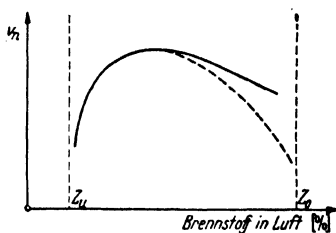
FIG. 62.—Forms of the burning cone. (From Ubbelohde and Koelliker.)

of the impulse to all sides takes place, and at some distance over the burner the distribution of the impulse is represented by the dotted line with the same direction of flow. The spread of the moving gas masses is caused solely by the induction of the outside air.

**4. Methodology for Determining Normal Combustion Velocity, According to Gouy and Michelson.**—In the investigations of the Karlsruhe Gas Institute, special attention was accorded the sources of possible error in the burner method. It is most convenient simply to measure the height of the cone  $h$ , together with the velocity of flow of the fresh gas. It is then possible to figure

the size of the cone surface if the radius of the burner is known, assuming an exact cone surface. From the size of the cone surface, the normal combustion velocity can be figured as the quotient of the flow volume per unit of time divided by the burning surface. This method is often adequate, since the deviations of the actual burning surface from the exact form of the cone are of such a nature that they are partly compensated for in relation to the entire surface (Fig. 62a). In extreme cases, however, burning surfaces of the form in Fig. 62b can appear.<sup>1</sup> In such cases one cannot simply measure the height; the flame must be photographed, and the size of the surface of revolution must be computed by a suitable numerical or graphic method. If this is not done, mistakes of up to 50 per cent can be made.

Another error that can be introduced in measurements by the cone method is the following: The ignition limits of gas mixtures are defined by the fact that a flame is just not able to propagate itself in them. Ubbelohde and Hofsäass (quoted page 72) had found that, although  $v_n$  trends to the value 0 at the lower limit of ignition, it does not do so at the upper limit (Fig. 63, in which the normal combustion velocity



(Brennstoff in Luft = fuel in air)

FIG. 63.—Normal combustion velocity as a function of the composition of the gas ( $Z_u$  and  $Z_o$  lower and upper ignition limits). Dashed line represents measurements with split-flame tube. (From Ubbelohde and Hofsäass.)

<sup>1</sup> Cf. UBBELOHDE, L., and E. KOELLIKER, quoted p. 79.

is schematically plotted against the fuel content in air.  $Z_u$  and  $Z_o$  are the lower and upper combustion limits). If one does not let the flame burn free, however, and employs instead a split-flame tube<sup>1</sup> (Fig. 64), the values at low fuel concentrations are the same with or without the use of the split-flame tube. At higher fuel concentrations, however, lower combustion velocities are found with the split-flame tube than without it. The reason for this is apparent: An adulteration of the fuel mixture by means of the surrounding atmosphere always occurs at the rim because of diffusion or possibly turbulence. If the surrounding element is air and if the fuel concentration is so high that the maximum of velocity has been passed, the combustion velocity is increased by the addition of air. In the split-flame tube, this cannot take place, because no fresh air is present.<sup>2</sup>

Recently, a detailed study of the burner method has been published by Smith and Pickering,<sup>3</sup> but no special attention was devoted to precisely this point. In the original work by Smith and Pickering, it was assumed that the velocity of the escaping gas was the same as that of the laminar flow in the burner tube. If the burning surface were a straight cone (at constant velocity of flow over the cross section), measurement (cf. page 71) of half the angular aperture  $\vartheta$  would serve to determine  $v_n$ . If the velocity is distributed over the cross section parabolically as in laminar flow, however, the burning surface has a different form and also a different average slope. There is, however, a point at a distance  $(\sqrt{2}/2)r_0 \approx 0.7r_0$  from the axis of the tube where  $v_f(r)$  is exactly equal to  $v_f$  and where as a result the element of the burning surface just under the angle  $\vartheta$  is inclined to the direction of flow (Fig. 65). The method of Smith and Pickering rests on determining the angle of slope at precisely this point and computing  $v_n$  from it. Obviously the method is lacking a sure theoretical basis (which Smith has begun to supply in his second work), since the distribution of velocity is different from that inside the burner tube. But, from the experiments reported on by Smith (and from the statements on "diffusion" of the impulse, page 67,



FIG. 64.—Split-flame tube, which prevents the entry of secondary air to the inner cone.

<sup>1</sup> This was first applied by N. Teclu, *J. prakt. Chem.*, **44**, 246 (1891) and then by A. Smithells and H. Ingle, *Trans. Chem. Soc.*, **61**, 216 (1892). Later F. Haber used the split-flame tube for his experiments on the composition of the "intermediate gas." The experiments with the split-flame tube are the first proof of the fact that the combustion in the inner cone of the Bunsen burner actually takes place in a very thin layer.

<sup>2</sup> Measurement even in the split-flame tube is not completely free from objections, since now, instead of air, diffusing combustion gases will reduce  $v_n$ .

<sup>3</sup> SMITH, F.A., and S.F. PICKERING, *J. Research Nat. Bur. Standards*, **17**, 7 (1936).

Fig. 61), it is clear that outside the burner in the center of the tube the velocity decreases and that it increases at the edge. Between these, there must be a section where the velocity has remained approximately constant. If Smith and Pickering have by chance measured in this section, the results obtained might under certain circumstances nevertheless be exact. Insofar as the method might prove effective in the future, it would have to be judged more as an experimental procedure for determining  $v_n$  than as a method with a sound theoretical basis. In his later work, Smith tends toward this view himself.

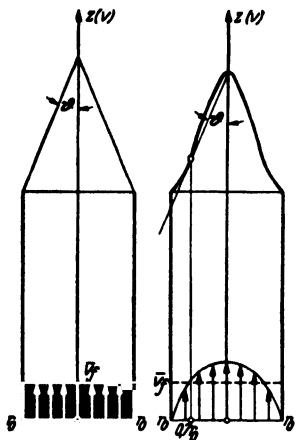


FIG. 65.—At  $r = 0.7 r_0$  (right) the burning surface has the same inclination  $\theta$  as a cone at a constant flow over the cross section of the tube. (From Smith and Pickering.)

ing surface increases with the square of the diameter of the burner, whereas the ring of disturbed combustion velocity adhering to the rim increases with only the first power of the radius. If we use the angular measurement of Smith and Pickering for measuring, we are working at a fixed distance from the rim, and it is possible that the effect of cooling as well as that caused by an induced mixing of secondary air is smaller here than it would be for the entire burning surface, inclusive of the rim. In Table 12, taken from Smith, results are shown as obtained from three different gas and air mixtures (air-lean, excess air, and a mixture of maximum combustion velocity) with four different burner diameters. In addition,  $v_n$  was computed in each case both for the angle  $r = 0.7r_0$  and for the extent of the entire burning surface.

Thus the following is clear: There are considerable discrepancies between the values for  $v_n$  computed according to Gouy (from the entire surface) and those according to Smith and Pickering. To be sure, these

A further factor that can fundamentally affect the burner method is what takes place at the tip and on the rim. At the tip (*cf.* page 79), the combustion velocity can be greater than normal; in the proximity of the mouth of the burner, it is certainly less because of the cooling effect of the burner; in the immediate proximity of the tube it is even zero. One will therefore be measuring, in general, an average combustion velocity, if it is measured from the burning surface and the volume of gas streaming through per second. The average velocity need not be identical with the normal combustion velocity. Probably it is somewhat less than the latter. It is clear from the start that the greater the diameter of the burner, the less will be the effect of possible disturbances; for the burn-

discrepancies decrease in each case as the radius of the burner increases. However, in column *A*, the change of  $v_n$  in respect to the radius is smaller for the value computed according to Gouy than for that computed according to Smith and Pickering. In the two following columns, the case is reversed. Furthermore, in column *A*, the combustion velocity decreases as the radius of the burner increases. These results can be understood very well on the basis of influences already recognized by

TABLE 12.—NORMAL COMBUSTION VELOCITY FOR THREE DIFFERENT GAS AND AIR MIXTURES AND DIFFERENT BURNER RADII. COMPUTED FROM THE INCLINATION OF THE BURNING SURFACE AT  $r = 0.7r_0$  AND FROM THE TOTAL BURNING SURFACE (FROM SMITH)

| Diameter of the burner                                  | Normal combustion velocity, cm/sec                          |   |
|---|---|---|
|   | From the inclination at $0.7r_0$ (from Smith and Pickering) | From the volume of flow per sec: flame surface (Gouy) |
| <i>Series A. Air Deficiency</i>                         |   |   |
| 2.75  | 27.9  | 18.5  |
| 4.45  | 24.2  | 16.8  |
| 6.50  | 17.4  | 15.1  |
| 9.60  | 14.4  | 13.8  |
| <i>Series B. Mixture of Maximum Combustion Velocity</i> |   |   |
| 2.75  | 47.2  | 29.0  |
| 4.45  | 53.5  | 38.0  |
| 6.50  | 53.4  | 43.8  |
| 9.60  | 53.6  | 47.7  |
| <i>Series C. Excess of Air</i>                          |   |   |
| 2.75  | 45.8  | 30.7  |
| 4.45  | 48.2  | 35.9  |
| 6.50  | 48.7  | 41.3  |
| 9.60  | 48.1  | 43.6  |

Ubbelohde. When air is absent, the greatest disturbing factor is the induced mixing of secondary air, which increases the combustion velocity considerably. Since, according to Gouy, the entire combustion surface is used, and, according to Smith and Pickering, only a portion is situated in the outer third, the disturbed portion contributes more to the total result in the latter case than in the former. In Cases *B* and *C*, an influence of the induced air could also be present, but it can only cause a lessening of the combustion velocity. In addition, according to Gouy, the cooling effect of the rim of the burner should be taken into account



in the computations, but this factor need not necessarily be of importance, according to Pickering and Smith, as has already been discussed. Moreover, systematic errors may have been introduced into the values obtained by Smith and Pickering, owing to the unfounded assumption regarding the condition of flow. To be sure, Smith mentions that the numbers thus computed agree with the results of Stevens. That speaks for their reliability but is not an absolute proof, since it is conceivable that the Stevens method yielded values that were too high because of a certain waviness of the burning surface.



FIG. 66. Forms of burning "cone" for various burner diameters (mm). Above, series A, air deficiency. Middle, series B, mixtures of maximum velocity. Below, series C, excess of air. [From Smith, *Chem Rev.*, vol. 21 (1937).]

constant. Figure 67 is better suited for purposes of comparison. Here all burning surfaces are so enlarged that the diameters of the burners appear equally large. These are drawn in according to their size and position (burner mouth). By this means, it is easy to recognize the relative position of the individual burning surface with respect to the mouth of the burner and the considerable widening of the base of the burning surface in relation to the mouth of the burner in burners with small diameters. From this (as well as from the older works of Ubbelohde), it is clear that the influence of secondary air added by induction is important.

The normal velocity of combustion is influenced relatively little by external factors like pressure and temperature. For example, Ubbelohde

For determining  $v_n$ , the following could be deduced from the older works of Ubbelohde: One should not work with too small a burner diameter and one should perhaps use a split-flame tube, especially with rich mixtures. For practical purposes, however, the effective combustion velocities of small burners can be of significance. In that case, it is exactly the observations given above which are of importance. It is of interest to call to mind the forms of the burning surface<sup>1</sup> (Figs. 66 and 67). Figure 66 shows the photographs of the burning surfaces for the three columns A, B, and C. In each column, temperature, pressure, composition, and velocity of flow are kept constant.

<sup>1</sup> Cf. also UBBELOHDE and DOMMER, as well as UBBELOHDE and KOELIKER, quoted p. 72.

and Hofsäss<sup>1</sup> found that, in carbon monoxide and air mixtures, a rise in temperature of 100° caused an increase in the velocity of combustion of 5 to 6 cm/sec. By preheating of 20° to 460°,  $v_n$  rose from 42 to 85 cm/sec. In mixtures of methane and air, 20°C yielded 31 and 430°C yielded 64 cm/sec.

Sachsse<sup>2</sup> finds for methane, ethane, and propane in mixture with oxygen a temperature dependence of the same order of magnitude.

The relatively small increase in combustion velocity with a rise in temperature has the following importance for the practical operation of a burner: If the combustion tube and thus the fresh gas are heated, the velocity of the fresh gas, because of volume expansion, increases

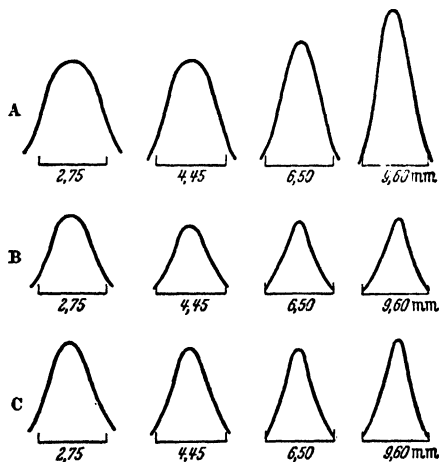


FIG. 67.—As in Fig. 66, from top to bottom, series A, B, C. However, for purposes of comparison the pictures with various burner diameters are so enlarged that the latter appear the same for all. Position and size of the mouth of the burner are indicated by horizontal lines. [From F.A. Smith, *Chem. Rev.*, vol. 21 (1937).]

more rapidly than  $v_n$ . As a result, the originally stable flame is, with rising temperature, finally blown away from the burner and does not “pop” (cf. Smith, cited page 83). In mixtures rich in oxygen and in burners that normally work at high temperatures, the situation can change.

Increase in pressure frequently decreases the normal velocity of combustion, at least as far as it is possible to draw conclusions from the measurements made thus far. Ubbelohde and Koelliker (cited page 72), for example, find that, in carbon monoxide and air mixtures of maximum combustion velocity, the combustion velocity  $v_n$  decreases from 42 to 24 cm/sec when the pressure is increased from 1 to 4 atm. In methane and air mixtures, a rise in pressure from 1 to 4 atm caused a 50 per cent

<sup>1</sup> UBBELOHDE, L., and M. HOFSSÄSS, *Gas- u. Wasserfach*, **56**, 1225, 1253 (1913).

<sup>2</sup> SACHSSE, H., *Z. physik. Chem., Sec. A*, **180**, 305 (1937).

decrease in combustion velocity. Acetylene and air were qualitatively the same. In benzol and benzene,  $v_n$  decreased only very slowly with the pressure. In hydrogen and air, the results were contradictory. With a burner radius of 0.95 mm,  $v_n$  increased considerably with the pressure; at 2 mm radius,  $v_n$  is about constant. Whether  $v_n$  would decrease with the pressure under smooth flow conditions is hard to predict.

Khitrin<sup>1</sup> has recently investigated the influence of the pressure on the velocity of combustion. He used the burner method as well as Stevens's soap-bubble method (the soap bubble was prepared on the inside of a 0.5 cu m pressure vessel). The results were as follows (in essential agreement with Ubbelohde): In fuel and air mixtures, the linear combustion velocity decreases with increased pressure. But, since it decreases less than  $1/p$ , the converted mass, in other words, the "mass conversion velocity," increases nevertheless with increasing pressure, as

$$m = K_1 \sqrt{p} + K_2$$

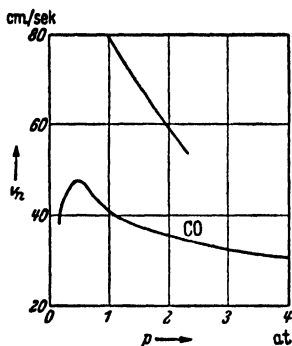


FIG. 68.—Dependence of the normal combustion velocity on the pressure for carbon monoxide and air, as well as acetylene (upper curve) and air mixtures. (From Ubbelohde and Khitrin.)

independent of the pressure. Results analogous to those obtained for carbon monoxide and air were also obtained by Khitrin for benzol-air and ethyl ether-air according to the burner method. Flame velocities at low pressure appear hardly to have been investigated,<sup>3</sup> except for carbon monoxide and air (Ubbelohde). A maximum combustion velocity results at a pressure of 330 mm Hg with about 60 cm/sec. After that  $v_n$  drops again with further decreasing pressure (Fig. 68). Apparently the factor of reaction velocity, which must have the effect of a decrease,<sup>4</sup> predominates at very low pressure.

<sup>1</sup> KHITRIN, L., *Tech. Phys. USSR*, **3**, 926 (1936). KOLODISEW, K., and L. KHITRIN, *Tech. Phys. USSR*, **3**, 1034 (1936). Cf. also KHITRIN, L., *Tech. Phys. USSR*, **3**, 1028 (1936); **4**, 110, 121 (1937).

<sup>2</sup> STEVENS, F.W., *NACA Rept.* 372 (1930).

<sup>3</sup> Cf. in this connection GARNER, W.E., and A. PUGH, *Trans. Faraday Soc.*, **35**, 283 (1939).

<sup>4</sup> G. RIBAUD and H. GAUDRY, *Compt. rend.*, **206**, 1648 (1938), found also for flame propagation in tubes, communicating with a large pressure vessel filled with nitrogen (for maintaining constant pressure), that with increasing pressure the flame velocity decreases. They worked with city gas and propane in the range of 1 to 11 kg/cm<sup>2</sup>.

$v_n$  is independent of the velocity of the fresh gas. If this velocity is permitted to be too high, however, and the turbulent region is reached, apparent increases in the combustion velocity are noted. This might, however, be due to an enlargement of the effective surface (*cf.* Ubellohde and Koelliker, cited page 72).

We shall return to the effects of the composition of mixtures and additions when we discuss the theory of combustion velocities. Because of certain practical considerations, we refer the reader to Smith (cited page 83).

**5. Propagation of Combustion in Tubes.**—We have noted that there is probably not a single case in which the propagation of a flame is

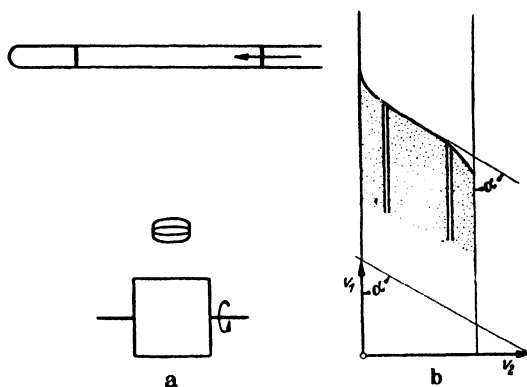


FIG. 69.—Photographic flame recording. *a*, sketch of the apparatus. *b*, photo. (From Mallard and Le Chatelier.)

determined solely by the normal combustion velocity. To be sure, it is possible to determine  $v_n$  from the size or the inclination of the static burning surface in the inner cone of a Bunsen flame, but the burning surface becomes static and takes on its characteristic form only through the joint effect of flow and combustion. In the “constant-pressure bomb” of Stevens, *i.e.*, in the soap-bubble method, the flame, it is true, spreads out in such a way that it is possible to compute  $v_n$  directly from it. But, again, the progress of the flame not only is given by  $v_n$  but is also determined by the expansion of the burned gases, in other words, by a flow process which in this case only (because of spherical symmetry and constant pressure) happens to be so simple that it can easily be computed.

All this is changed as soon as one proceeds to combustion chambers of a different type. We shall consider only open chambers in this chapter, because we want to operate, at least for the present, with practically constant pressure. The method most commonly employed for determining flame velocities is the photographic procedure introduced by

Mallard and Le Chatelier<sup>1</sup> (Fig. 69). The tube in which the flame travels is thrown on a film by means of a photographic lens. The film is on a drum rotating at a known rate of speed. The flame image thus obtained is schematically represented by Fig. 69b. The angle  $\alpha$  of inclination which the path of the flame front forms with the direction of the film movement bears, at any point, the following relation to the velocity of the film  $v_1$  and the velocity of the flame image on the film  $v_2$ :

$$\tan \alpha = \frac{v_2}{v_1}$$



FIG. 70—Photographs of a uniform flame movement [From Maxwell and Wheeler, *The Science of Petroleum*, vol. IV, Oxford (1938)]

the marks on the flame image. Original photographs by Mallard and Le Chatelier are reproduced in Chap. V. By way of explanation, two typical flame pictures are reproduced here (Figs. 70 and 71), of which the first shows a completely uniform movement and the second a movement with marked oscillations. In the latter, however, the movement in the center is still approximately uniform. The structure of the flame front becomes somewhat clear if snapshots are made of it. Since the position of the flame front constantly changes during the progress of the flame, an entire series of snapshots can be made, one after another, on the same fixed plate. Ellis<sup>2</sup> in particular has made extremely instructive flame pictures

Since  $v_1$  is known and  $\alpha$  can be measured directly on the negative,  $v_2$  is easily computed. In order to convert the velocity of the flame image to the flame itself, it is necessary to know the scale of the optical equipment used. The simplest and most exact method for this is to put two or more dark marks on the flame tube (Fig. 69), which in some instances are already present in the construction of the tube (e.g., a metal tube with windows), or by the holder (in the case of glass tubes). These marks then form on the negative as two bright stripes parallel to the movement of the film.  $v_2$  is then to be enlarged in the ratio distance of the marks on the tube divided by the distance of

<sup>1</sup> MALLARD and LE CHATELIER, *Ann. mines* (4), **8**, 274-618 (1883).

<sup>2</sup> Cf. in this connection ELLIS, O.C. DE C., and W.A. KIRKBY, "Flame," Methuen,

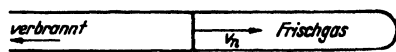
in this manner by fixing a rotating disk at a known velocity before the objective of a camera. Through slits in this disk, he regulated the illumination for the individual pictures. Similar pictures by H. Schulze made for closed vessels with Thun's high-speed camera are reproduced in the following chapter. We shall return later to experiments by Coward and Hartwell which were made by the same method. It is particularly clear from these photographs that the burning surface of



FIG. 71.—Flame movement with overlapping oscillations. (From Benec-Tournend, *Flame and Combustion*.)

flames in tubes is never a plane and that as a result the flame velocity can never be given by  $v_n$ . In the following, we shall consider qualitatively what kind of currents should be studied. We shall particularly see that, also in the apparently static fresh gas before the flame front, currents must occur, since otherwise an uneven burning surface could not be static at all. As we shall see, no case can be cited (except in the spherical-symmetrical case to which also belongs the unimportant borderline case of an infinitely extended gas mass with a plane burning surface) in which the form of the burning surface would not be essentially modified by gas currents.

One might at first expect that in a cylindrical tube a plane burning surface perpendicular to the axis of the tube could be stable, as in Fig.



(verbrannt = burned)  
(Frischgas = fresh gas)

FIG. 72.

72. This burning surface would have to move forward with the normal combustion velocity  $v_n$  relative to the unburned gas. At first, a certain flow must always be present on account of the expansion of the burned gas (cooling by radiation and conduction to the outside should be disregarded at first). This flow will be relatively easy to observe if, according to Fig. 72, we assume a moderately long tube closed at one end and ignited at the other. This is the standard method for determining the uniform flame velocity. Then the fresh gas would remain

London, 1936. ELLIS and ROBINSON, *J. Chem. Soc.*, 1925, p. 760. ELLIS and WHEELER, *J. Chem. Soc.*, 1925, p. 764; 1927, p. 310; 1928, p. 3215; 1931, p. 2467. ELLIS, *Fuel*, **7**, 195, 245, 300, 336, 408, 449, 502, 526 (1928); *Phot. J.*, **67**, 349 (1927); **72**, 380 (1932); **74**, 404 (1934); **75**, 482 (1935).

practically static, and the burned gases would flow off to the left. We shall assume that the conditions for laminar flow are fulfilled for the burned gas.<sup>1</sup> In that case, a parabolic velocity distribution would exist over the cross section of the tube, and in the absence of slipping the immediate edge zone would contribute very little to oblique flow. In any case, more gas will flow through a cross section close to the center of the tube than in one of the same area close to the edge. On the other hand, assuming a plane burning surface, the same amount of gas per unit of square surface will be converted everywhere. Thus, in general,

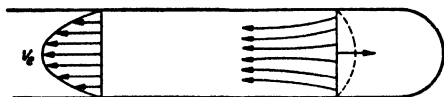


FIG. 73.—Discharge of the burned gases with flame progressing in a tube open at one end.

a flow as represented in Fig. 73 would qualitatively result; *i.e.*, the current coming from the burning surface would have to converge toward the center of the tube. It is not self-evident to assume a plane burning surface; one could also imagine that the burning surface might approximate the dashed curve in Fig. 73.

The experiments actually show that the flame front is approximately semispherical during the stage of uniform flame velocity. To be sure, the conditions (*cf.* Coward and Hartwell, cited page 97) are still too much idealized, since, especially in horizontal tubes, added asymmetrical distortions appear as the result of gravity.<sup>2</sup>

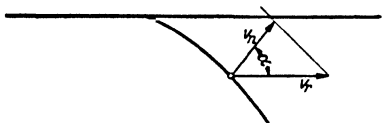


FIG. 74.—Progression velocity  $v_r$  of a burning surface inclined toward the axis of the tube ( $v_n$ , normal combustion velocity).

Let us assume a semispherical burning surface as the approximate result of the experiments. If a plane burning surface could have been static, it would have shifted exactly with the normal combustion velocity (confining disturbances are to be disregarded for the present). If, then,  $r_0$  is the radius of the tube, the quantity of fresh gas  $\pi r_0^2 v_n$  would be converted per unit of time. In the case of a semispherical burning surface, the gas quantity  $2\pi r_0^2 v_n$  would be converted in the same time. The burning surface assumed as static must thus move toward the fresh gas with the velocity  $2v_n$ , which is possible only with the assistance of a circulation in front of the flame front. How that takes place will have to be taken up in greater detail later. First it is clear, on

<sup>1</sup> An even, smooth, burning surface could in no way be assumed for turbulent flow.

<sup>2</sup> In this discussion, we shall for the time being disregard the effects of gravity. These also cause differences in the flame velocity depending on the position of the tube (horizontal or vertical) and the direction of the flame movement in the vertical tube (upward or downward).

the basis of what has been said, that the resulting propagation velocity in the direction of the tube axis  $v_r$  (still excluding flow, of course, and for an element of the burning surface whose normal is directed to the fresh gas with the direction of  $v_r$  and includes the angle  $\alpha$ ) is given by (Fig. 74)

$$\frac{v_n}{v_r} = \cos \alpha \quad v_r = \frac{v_n}{\cos \alpha}$$

Everywhere, therefore, where the burning surface is not perpendicular to the tube axis,  $v_r > v_n$ ;  $\alpha = 0$  only in the axis, and the flame velocity equals  $v_n$ . The result would therefore be a rush forward of the retarded rim portions until finally the burning surface would have changed over into a plane with a resulting propagation velocity equal everywhere. It should be noted that this is true only if all flow is excluded. If a plane burning surface cannot be stable and if, on the other hand, a distorted burning surface would be compelled to change over into a plane perpendicular to the axis of the tube (no flow being present in the fresh gas), it would follow that currents must exist also in the fresh gas. We shall attempt to visualize these currents.

In itself the problem should, of course, be stated in reverse. The condition of flow and the form of the burning surface are to be obtained from the given normal combustion velocity and the hydrodynamic laws for flow. Remarkably enough, the problem does not yet appear to have been treated in this form in the literature of the field. We shall therefore dispense with a more exact treatment and content ourselves with gaining an insight into the flow conditions, assuming a plausible form of the burning surface. To be sure, we shall see even here that—at any rate if we assume a constant combustion velocity everywhere—a semi-spherical burning surface cannot be stationary; for, with a semispherical burning surface,  $\alpha$  at the rim would be equal to  $\pi/2$ , in other words  $v_r = \infty$ . The resulting infinite propagation velocity would have to be compensated for by a similarly infinitely rapid flow of the fresh gas in the opposite direction,<sup>1</sup> which is absurd. Therefore only one burning surface cutting the tube wall at an acute angle can be stable at constant normal combustion velocity.<sup>1</sup> As the simplest surface meeting this requirement, let us take the paraboloid of revolution which has the same height as the hemisphere and therefore also a similar surface (Fig. 75), i.e., the paraboloid

$$z = -\frac{r^2}{r_0} \quad (24)$$

Since the paraboloid surface is 1.86 times that of the tube cross section,

<sup>1</sup> The conditions change if we take the cooling effect of the wall into consideration. Then this difficulty disposes of itself, but other difficulties, from which we wish to free ourselves for the present discussion, remain at the rim.



the flame velocity must be 1.86 times the normal velocity of combustion. In the tube center (Fig. 75), where the burning surface is perpendicular to the tube axis, the resulting combustion velocity must be the value  $v_n$ ; therefore an added forward flow,  $(1.86 - 1)v_n = 0.86v_n$ , must be present in the fresh gas in order to obtain the effective flame velocity  $v_{\text{eff}} = 1.86$ . To the same degree, progressing from the tube axis, the resulting combustion velocity,  $v_r = v_n / \cos \alpha$ , increases until a point is finally reached where  $v_r = v_{\text{eff}} = 1.86v_n$ ,  $\cos \alpha = 1/1.86$ . Here, then, the flow component in the direction of the tube axis is equal to zero. Still farther outward,  $v_r > v_{\text{eff}}$ ; here a flow against the flame front exists which again makes the effective flame velocity uniformly equal to  $v_{\text{eff}} = 1.86v_n$ . This flow conducts the necessary fresh gas to the "wedge" at the rim in order

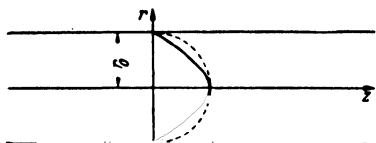


FIG. 75.—Idealized form of the burning surface (of paraboloid rotation).

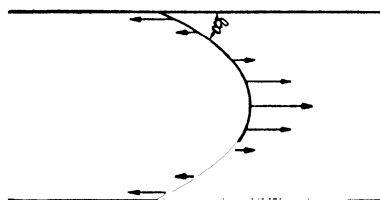


FIG. 76.—Axial flow components in the fresh gas in front of the (idealized) burning surface.

to hold the burning surface static in its form. Thus the flow velocity remains finite at the rim also, namely,  $v_n / \cos \alpha = 1.86v_n$ . In general, the schematic drawing of Fig. 76 shows what occurs in the fresh gas. Here the axial flow components of the fresh gas are drawn in immediately before the flame front.<sup>1</sup>

If  $E$  is the expansion ratio during combustion, the burned gases after passing through the burning surface attain a relative velocity perpendicular to the surface (cf. page 67)

$$v = -(E - 1)v_n^*$$

Since this velocity component is directed perpendicular to the burning surface, the direction of flow can penetrate the burning surface con-

<sup>1</sup> The value 1.86 is naturally connected with the selected illustration. It is generally noted that  $v_{\text{eff}}$  is at least about  $2v_n$ .

At any rate, attention is called to the fact that a flow like that pictured in Fig. 76 according to Hettner, *Ergeb. exakt. Naturw.*, 7 (1928), is obtained as the result of thermal slip according to Knudsen. If one inserts the values of the temperature drop valid for the burning zone ( $10^\circ\text{C}/\text{cm}$ ) into Hettner's formulas, one obtains at the wall of the tube a flow of  $\sim 10^2$  cm/sec directed against the hot gas. Unfortunately, in the case of flames, the transition layer toward the cold wall complicates the problem to such an extent that it is not even certain whether the effect can stand qualitatively. Nevertheless we call attention to these phenomena.

\* We use the minus sign because the direction of  $v$  is the opposite from that of  $v_r$ .

stantly only if it is vertical to the latter. Insofar, however, as the fresh gas flows against the burning surface at a certain angle, this direction is changed in the burning surface (exactly as in combustion in the Bunsen burner). The value of the velocity naturally changes irregularly in any case by passing through the burning surface. Whatever can be said qualitatively about flow conditions on the basis of the foregoing is graphically presented in Fig. 77*a, b, c*. From the foregoing, it is also immediately clear that it makes a difference if the velocity of the progress

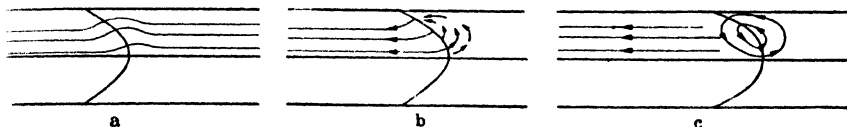


FIG. 77.—Flow with flame propagation in a tube. *a*, in reference to the burning surface. *b*, in reference to the tube. *c*, flow interpreted as overlapping of almost axial flow and of an eddy at the burning surface.

of the flame toward the static fresh gas in the tube is measured or if the flame is made static by a suitable counterflow of the fresh gas. The velocity distribution in the tube is thus different from that prevailing in the static fresh gas; thereby the flame front must take on a different form and surface, and thus the effective flame velocity is changed.

If we considered the cooling effect of the wall that would result in a lowering of the normal combustion velocity (not yet investigated in detail), the form of the burning surface toward the rim would be essentially different from the parabola in the sketch. If the normal combustion velocity at the rim approaches zero,  $\cos \alpha$  would have to approach zero in the immediate proximity of the rim in order that  $v_r = v_n / \cos \alpha$  would remain finite, and one would obtain a "curling in" at the rim, which observation seems to confirm (Fig. 78), where the flame ceases some distance from the rim.



FIG. 78.—Flame form, with cooling due to the wall taken into account.

Examples showing the form of burning surfaces actually observed are shown in Fig. 79. One can also attempt, as Coward and Hartwell have,<sup>1</sup> to compute the size of the flame surfaces in a tube from the photographs by assuming a simple geometric form, *e.g.*, an ellipsoid (as the result of gravity, no rotational symmetry is present in the horizontal tube). If one lets the converted gas quantity equal the cross section of the tube,  $\pi r^2$ , times the observed flame velocity  $v_{\text{eff}}$ , and as likewise equal to the actual burning surface  $f$  times the normal combustion velocity  $v_n$

$$\pi r^2 v_{\text{eff}} = f v_n \quad (25)$$

<sup>1</sup> COWARD, H.F., and F.J. HARTWELL, *J. Chem. Soc.*, 1932, p. 2676.

| Direction of movement               | Horizontal | Upward | Downward | Horizontal |
|-------------------------------------|------------|--------|----------|------------|
| Diameter of the tube, cm            | 2.5        | 5      | 5        | 10         |
| Interval between two pictures, sec. | 36         | 18     | 73       | 97         |

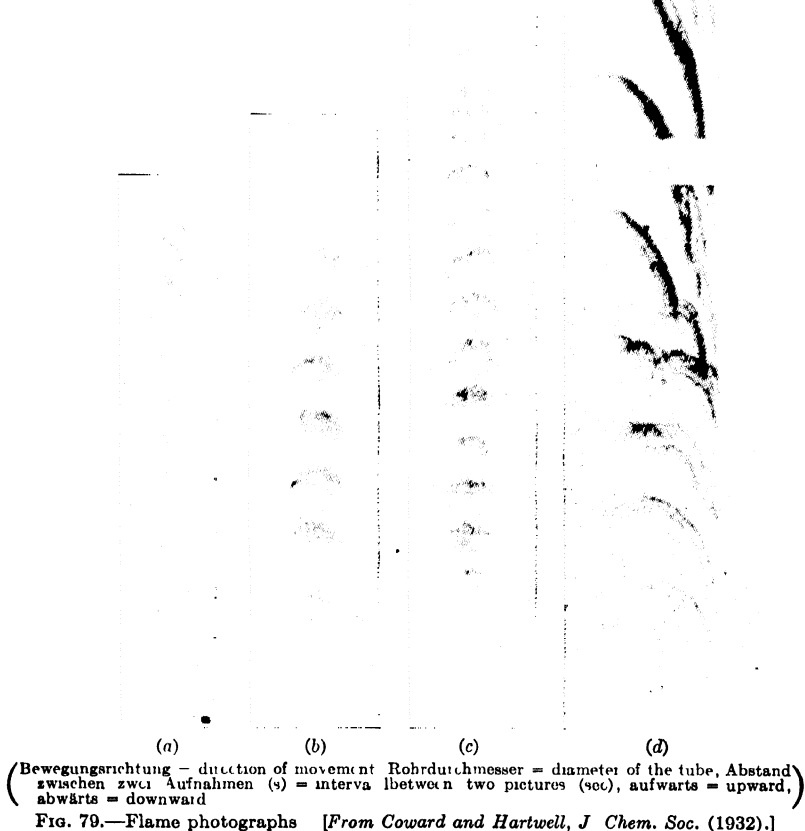
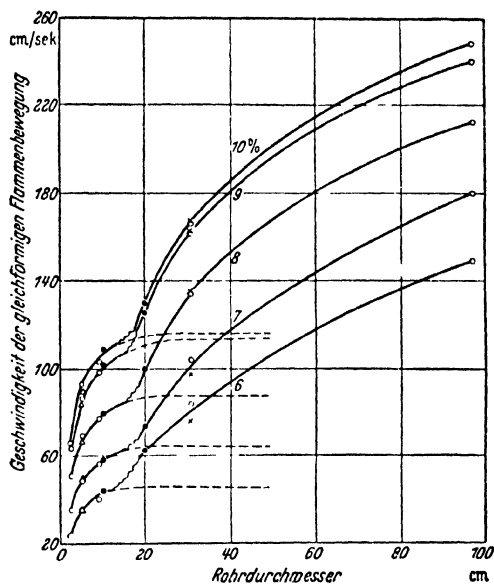


Fig. 79.—Flame photographs [From Coward and Hartwell, *J. Chem. Soc.* (1932).]

one obtains a relation in which all the entities except  $v_n$  are directly measured and which therefore makes it possible to compute  $v_n$ . In Fig. 79, we offer photographs by Coward and Hartwell which have been used in the manner indicated above. If the diameter of the tube or the flame velocity is too large, the method is no longer applicable because the burning surface has no simple form but rather becomes irregular, which incidentally gives a natural explanation for the rise in flame velocity observed in such cases. We reproduce the results of Coward and



(Geschwindigkeit der gleichförmigen Flammenbewegung = velocity of the uniform flame movement)  
(Rohrdurchmesser = diameter of the tube)

FIG. 80.—Flame velocities of various methane and air mixtures (% methane) in dependence on the diameter of the tube. [From Coward and Hartwell, *J. Chem. Soc.* (1932) p. 1999.]

Hartwell for a 10 per cent mixture of methane and air in Table 13. It is clear that, from flame velocities that vary considerably (about 1:2) with the diameter of the tube, position of the tube, and direction of motion of the flame, combustion velocities can be computed that deviate by only a few per cent from the average, which in its turn is in tolerable agreement with values obtained from the burner method. One sees, by the way, that the flame velocity in tubes is always at least double the normal combustion velocity.

The flame velocity generally increases with increased tube diameter, as can be seen from Table 13. Systematic results, likewise from Coward and Hartwell, are given in Fig. 80.

TABLE 13.—FLAME VELOCITIES OF A 10 PER CENT MIXTURE OF METHANE-AIR IN TUBES OF VARIOUS DIAMETERS. ALSO COMBUSTION VELOCITIES COMPUTED FROM THEM (FROM COWARD AND HARTWELL)

| Diameter of tube, cm | Flame movement | Axial flame velocity, $v_{\text{eff}}$ cm/sec | Flame surface, cm <sup>2</sup> | Normal combustion velocity according to Eq. (25), cm/sec |
|----------------------|----------------|---|--------------------------------|--|
| 10                   | Horizontal     | 111   | 300                            | 29   |
| 10                   | Horizontal     | 71  | 189                            | 29   |
| 5                    | Horizontal     | 92  | 66                             | 27   |
| 5                    | Horizontal     | 61.5  | 48.5                           | 25   |
| 2.5                  | Horizontal     | 71.5  | 12.6                           | 28   |
| 2.5                  | Horizontal     | 63  | 11.0                           | 28   |
| 2.5                  | Horizontal     | 59  | 10.4                           | 28   |
| 2.5                  | Upward         | 68  | 48                             | 28   |
| 2.5                  | Upward         | 92.5  | 66.5                           | 27   |
| 2.5                  | Downward       | 61  | 46                             | 26   |
| 2.5                  | Downward       | 58  | 63.5                           | 26   |

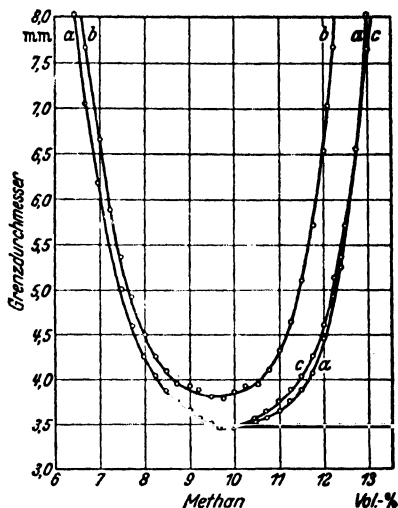
If the diameter of the tube is decreased still further, the flame velocity decreases more and more until, at a finite, small diameter (generally of the order of magnitude 1 mm), a flame does not propagate at all. Qualitatively the effect can be readily understood. As the result of heat loss to the wall, the combustion velocity must decrease toward the rim, and in the immediate proximity of the wall it will be practically zero. We have seen above (page 97) that in larger tubes the flame can curl inward at the rim. The practical result is that a certain layer adjacent to the wall is not reached by the flame at all (which does not mean, of course, that this portion of the gas is not burned. The influence of diffusion alone would cause it to mix with the burning gases behind the flame front where it would be subject to reaction). If one now imagines a tube in which there is a narrow annular portion untouched by the flame, and if one imagines this tube becoming smaller and smaller, then the ring must finally occupy the entire cross section of the tube without leaving any space for the flame surface; *i.e.*, a flame can no longer propagate in the narrow tube. One could now assume that the minimum diameter of a tube through which a flame would still be propagated would depend considerably on the material of the tube wall because of varying conductivity. This is, however, not the case.<sup>1</sup> The minimum diameter of a tube in which a flame is still able to propagate was found, within limits of error of 2.5 per cent, to be the same for glass and copper, although the heat conductivities are in the relation of 1:460.

Numerical values for diameter limits (Fig. 81) according to Holm are given for methane and air. They amount to several millimeters. For

<sup>1</sup> HOLM, J.M., *Phil. Mag.*, **14**, 18 (1932); **15**, 329 (1933).

illuminating gas, the values are lower, and they are still lower for hydrogen.<sup>1</sup>

If one gives the matter more thought, this is not at all surprising; for the heat capacity, as well as the conductivity, of the wall material is always—but especially in tubes of narrow inside width, with which we are especially concerned here—relatively great in comparison with that of the burning gases. Moreover, since heat conduction comes into play only in the short time during which the burning zone passes by a point, the wall will never be very much heated. As a result, thermal capacity and conductivity of the wall can play only a subordinate role in influencing the flame. Therefore the following situation presents itself: The flame has at first a semispherical form and does not itself come in contact with the wall anywhere. The ratio of the heat produced within this hemisphere by combustion to the heat flow permeating the surface of the hemisphere grows less favorable the smaller the radius of the sphere becomes; the flame will therefore be extinguished below a certain radius. In this form, the problem has been stated by Holm (cited page 100), who emphasizes on the one hand the analogy with spark ignition as long as the latter is regarded as a thermal phenomenon (*cf.* page 49), and on the other hand points out that in reality the flame is cooled off not by the wall itself at all but by the fresh gas in front of it. The wall merely determines the size and form of the burning surface as well as the temperature of the fresh gas. Occasional observations on differences in the velocity of flames in tubes of various materials are probably to be evaluated differently. The condition of the wall (let us say, a rough, oxidized metal surface as opposed to a smooth glass wall) influences the condition of flow of the gas and hence indirectly the flame



(Grenzdurchmesser = diameter limit)

FIG. 81.—Diameter limit for methane and air mixtures below which flames no longer propagate. *a*, hole in copper foil. *b*, copper tube. *c*, copper foil (other method). [From Holm, *Phil. Mag.* (7), vol. 14 (1932).]

<sup>1</sup> Studies on ignition penetrating through narrow slits with respect to the use of electrical apparatus in industries endangered by explosion were made by D. Müller-Hillebrand, *Elektrotech. Z.*, **59**, 1116 (1938). In methane, a slit length of 25 mm with a width of 1.15 mm was still safe, whereas in acetylene a reduction to 0.02 had to be reached. In general, it should be borne in mind that the greater the movements of the gas as a whole the more readily will a flame penetrate a narrow tube or slit.

velocity. In Table 14, taken from Bone ("Flame and Combustion"), we give a compilation of values for the flame velocity of methane-air mixtures in four tubes, according to experiments by Parker and Rhead. The small differences appearing in the flame velocities in glass, lead, copper, and iron tubes can largely be regarded as the result of the differences in the diameters. At any rate, there is no valid reason for thinking of the flame velocity as being influenced by the thermal capacity and conductivity of the wall.

TABLE 14.—FLAME VELOCITIES (IN CM/SEC) OF METHANE AND AIR MIXTURES IN FOUR DIFFERENT TUBES, ACCORDING TO PARKER AND RHEAD (FROM BONE)

| % methane | Glass tube<br>2.65 cm diam | Lead tube<br>2.64 cm diam | Copper tube<br>2.2 cm diam | Iron tube<br>2.72 cm diam |
|-----------|----------------------------|---------------------------|----------------------------|---------------------------|
| 5.99      | 21.7                       | 19.4                      | 18.3                       | 21.2                      |
| 6.83      | 33.4                       | 32.5                      | 32.7                       | 34.1                      |
| 7.6       | 45.6                       | 43.5                      | 42.4                       | 43.8                      |
| 7.95      | 48.6                       | 48.2                      | 45.2                       |                           |
| 8.94      | 63.66                      | 58.7                      | 59.4                       | 63.3                      |
| 10.0      | 69.8                       | 65.0                      | 63.2                       | 67.3                      |
| 10.98     | 61.1                       | 53.9                      | 54.1                       | 57.5                      |
| 11.3      | 53.3                       | 45.4                      | 47.7                       | 50.6                      |
| 11.74     | 36.9                       | 35.2                      | 34.5                       | 36.1                      |

One could now ask how these facts can be brought into harmony with the fact that, since Davy, a wire netting<sup>1</sup> of high conductivity has been used to prevent penetration by a flame. In this case, the conductivity of the material plays a decisive role. It must be borne in mind that one is dealing here with two different problems. In the case of Davy's wire netting, the flame burns statically above the netting. If the wire netting did not conduct any heat, it would in time certainly be heated to the ignition temperature of the gas, and the flame could go through. In the case of a flame progressing in a tube or a flame that is extinguished because the diameter of the tube is too small, the flame is at all times only briefly in contact with each element of the tube. It is different if one makes the flame stationary by letting the gas flow counter to the flame travel. In that case, the tube can heat up more at the location of the flame, and thermal conductivity must play an essential role.

Several more quantitative estimates of the above statements will be made later in connection with the theory of combustion velocity.

From the general observation that, except in very narrow tubes, the flame velocity never remains stationary (*cf.* page 162) for long

<sup>1</sup> DAVY, H., Ueber die Sicherheitslampe, *Ostwalds Klassiker* 242. The problem of thermal conductivity in Davy's wire netting has been treated by Mache (cited p. 70).

distances (*i.e.*, several meters), it can be concluded that the flame propagation hitherto discussed cannot be absolutely stable. On the other hand, it is remarkable that, for the initial stage, assuming that certain precautions are taken, flame velocities can be obtained which can be reproduced easily. This and the fact that flame pictures like those in Fig. 71, page 93, can be obtained in which the flame vibrates for reasons not yet known in detail but in which, even during the stage of vibration, the average flame velocity remains the same as in the preceding stage of uniform motion—these facts speak for the stability of the flame movement with sufficiently small disturbances. To be sure, in the case of vibrations of greater amplitude, changes of flame velocity are always present, and sometimes these changes are quite considerable.

In the transition from a stage of uniform flame velocity, there is often a range of vibrations. Why the vibrations set in and how they arise

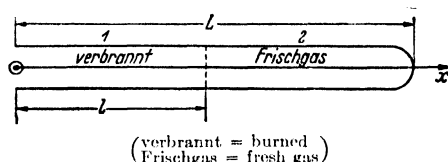


FIG. 82.

seems not to have been studied as yet; only data on their characteristic frequency are available. At any rate, it seems that, in a gas that is in a tube and is ignited at the open end, the vibrations begin most readily and are of the greatest amplitude, if a mixture with excess fuel is present which mixes with the secondary air when leaving the tube and continues to burn. It is quite likely that the reaction of this secondary combustion causes the vibrations and amplifies them.

If, as is reasonable, the vibration stage is regarded as the usual motion of the flame, to which is added the vibration of the gas mass as a whole, it is simply a matter (Fig. 82) of computing the characteristic frequencies of a column of gas in a tube open at one end, the gas consisting partly of fresh gas and partly of burned gas. This is nothing more than the problem of the open tube except that the column of air consists of two layers that have different chemical compositions, temperatures, densities, and therefore also different adiabatic compressibilities.<sup>1</sup> It will be expected in advance—and the computations confirm this—that the frequencies lie between those valid for the pure fresh gas and those of the pure exhaust gases.

Referring to Fig. 82, let  $\xi$  be the displacement of a particle in the  $x$ -direction. We thus get the differential equation<sup>2</sup>

<sup>1</sup> Cf. also ELLIS and KIRKBY, "Flame." LEES, C.H., *Proc. Phys. Soc. London*, 41, 204 (1929).

<sup>2</sup> Cf. textbooks in physics.



$$\frac{\partial^2 \xi_1}{\partial t^2} = c_1^2 \frac{\partial^2 \xi_1}{\partial x^2}; \quad \frac{\partial^2 \xi_2}{\partial t^2} = c_2^2 \frac{\partial^2 \xi_2}{\partial x^2} \quad (26)$$

in which the subscripts 1 and 2 designate the burned and the unburned gas, respectively, and  $c$  is the velocity of sound applying. Also the following comes into consideration:

$$c_1^2 = \left( \frac{dp}{d\rho} \right)_1 \quad c_2^2 = \left( \frac{dp}{d\rho} \right)_2$$

$$c_1^2 = \frac{p_1 \kappa_1}{\rho_1} \quad c_2^2 = \frac{p_2 \kappa_2}{\rho_2} \quad (27)$$

in which  $p$  is the pressure,  $\rho$  the density,  $\kappa$  the relation of the specific heats ( $= c_p/c_v$ ), and the subscripts 1 and 2 have the same meaning as above.

Furthermore, the following boundary conditions must be fulfilled: At the right, or closed, end of the tube, for  $x = L$  there must be a node, *i.e.*, the displacements of the gas particles must be 0 there; in other words  $\xi_1$  or  $\xi_2 = 0$ . Conversely, maximum amplitude must be present at the left open end; *i.e.*, the displacement must take place there entirely unhindered.<sup>1</sup> Here the outer atmospheric pressure prevails as a constant, and  $\partial \xi / \partial x = 0$ . We thus formulate both boundary conditions

$$(a) \quad \xi_1 = 0 \quad \text{or} \quad \xi_2 = 0 \quad \text{for } x = L$$

$$(b) \quad \frac{\partial \xi_1}{\partial x} = 0 \quad \text{or} \quad \frac{\partial \xi_2}{\partial x} = 0 \quad \text{for } x = 0 \quad (28)$$

A particular integral that fulfills both the differential equation and each of the two boundary conditions is

$$\xi_1 = a_1 \cos \frac{2\pi \nu x}{c_1} \cos 2\pi \nu t$$

$$\xi_2 = a_2 \sin \frac{2\pi \nu (L - x)}{c_2} \cos 2\pi \nu t \quad (29)$$

Of this,  $\xi_1$  automatically fulfills the boundary condition at the left end,  $\xi_2$  that at the right end. If the tube is entirely filled with fresh gas at 2 or with burned gas at 1, the boundary conditions must first be fulfilled; *i.e.*, if we designate the frequencies appearing in these two cases with  $\nu_1$  and  $\nu_2$ , the following holds:<sup>2</sup>

$$(a) \quad \xi_1 = 0 \quad \text{for } x = L$$

$$(b) \quad \frac{\partial \xi_2}{\partial x} = 0 \quad \text{for } x = 0 \quad (30)$$

From this follows

$$(a) \quad \cos \frac{2\pi \nu_1 L}{c_1} = 0 \quad \text{or} \quad \frac{2\pi \nu_1 L}{c_1} = \frac{\pi}{2}$$

$$(b) \quad \cos \frac{2\pi \nu_2 L}{c_2} = 0 \quad \text{or} \quad \frac{2\pi \nu_2 L}{c_2} = \frac{\pi}{2} \quad (31)$$

That is

$$c_1 = 4\nu_1 L \quad c_2 = 4\nu_2 L \quad (32)$$

<sup>1</sup> In the analogous computations for tube vibrations, it is shown that a certain correction is to be made which takes care of the transition from the tube into free space. Cf., for example, "Handbuch der Physik," Vol. 8. We shall disregard these details.

<sup>2</sup> That harmonics also appear will be disregarded here. The appearance of harmonics can be seen especially well in direct shadow pictures of vibrating flames by A.G. White, *J. Chem. Soc.*, 1928, p. 1159.

Instead of (29), one can also write

$$\xi_1 = a_2 \cos \frac{\pi \nu x}{2\nu_1 L} \cos 2\pi \nu t \quad \xi_2 = a_2 \sin \frac{\pi \nu (L - x)}{2\nu_2 L} \cos 2\pi \nu t \quad (33)$$

In the place  $x = 1$ , displacement components and power components are assumed to be equal for both media. That yields

$$\begin{aligned} \xi_1 &= \xi_2 \\ \frac{\partial \xi_1}{\partial x} c_{1\rho_1}^2 &= \frac{\partial \xi_2}{\partial x} c_{2\rho_2}^2; \quad \frac{\partial \xi_1}{\partial x} p_{1\kappa_1} = \frac{\partial \xi_2}{\partial x} p_{2\kappa_2} \quad \text{for } x = l \end{aligned} \quad (34)$$

therefore

$$\begin{aligned} (a) \quad a_1 \cos \frac{\pi \nu l}{2\nu_1 L} &= a_2 \sin \frac{\pi \nu (L - l)}{2\nu_2 L} \\ (b) \quad \frac{p_{1\kappa_1} a_1}{\nu_1} \sin \frac{\pi \nu l}{2\nu_1 L} &= \frac{p_{2\kappa_2} a_2}{\nu_2} \cos \frac{\pi \nu (L - l)}{2\nu_2 L} \end{aligned} \quad (35)$$

If we disregard the difference between  $p_1$  and  $p_2$  (which is very slight in ordinary flames), division of (35b) by (35a) yields the equation for the vibration frequency

$$\frac{\kappa_1}{\nu_1} \tan \frac{\pi \nu l}{2\nu_1 L} = \frac{\kappa_2}{\nu_2} \cot \frac{\pi \nu (L - l)}{2\nu_2 L} \quad (36)$$

This relation has proved to be sound. The conditions (31) correspond to the assumption, by the way, that only the basic tones are stimulated. One can compute also for harmonics that are actually stimulated, perhaps the more so, the more intensive the vibrations.

The fact that the average flame propagation can be stationary for minute disturbances but not in vibrations of great amplitude is qualitatively a relatively simple observation (Fig. 83). For small vibrations (Fig. 83a), the flame surface will be slightly enlarged or reduced in vibrating back and forth. It may be, however, that



FIG. 83.

as an average the surface of the vibrating flame varies only slightly from that of the nonvibrating flame, and that as a result the average propagation velocity will also remain about the same. If the flame vibrates in large amplitudes (Fig. 83b), however, its average surface must always be greater than without vibration. But that means that the propagation velocity must also be increased, which leads to an increasing disturbance of the originally uniform flame movement, and finally (in addition to intermediary retardations) to an acceleration that under certain circumstances can lead to detonation. We shall see later (Chap. IV, page 144) that under special circumstances much more complicated flame forms can appear than are shown in Fig. 83.

**6. Theory of Flame Propagation.**—In the theoretical treatment of flame propagation, the situation resembles that of interpreting the

phenomena of auto-ignition and of spark ignition. We have simply assumed as self-evident that it was a matter of pure thermal processes and, proceeding from this assumption, have attempted to arrive at expressions for the normal velocity of combustion in more or less close approximation. Comparison of these expressions with experience (insofar as a comparison is possible considering the incompleteness of the theory) shows that, although some facts can be understood on the basis of the theory of heat, in others, discrepancies of a fundamental nature occur that demand a change in the theoretical foundation. Again it is a matter of taking into consideration the participation in the reaction of active particles, diffusion in general, and free atoms and radicals in particular.

If we nevertheless first briefly discuss the pure theory of heat, we do so because it represents a simple borderline case of the more complicated general problem, and because we can gain an insight into the complex phenomenon most easily by considering the more simple borderline case.

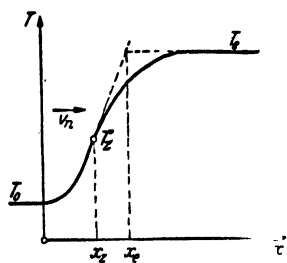


FIG. 84.—Temperature distribution in the burning zone.

The first attempt to establish a theory of heat for the normal combustion velocity was made by Mallard and Le Chatelier.<sup>1</sup> If we observe the structure of the burning zone of a flame (Fig. 84), the following becomes clear: We have given the temperature in the figure as the function of the distance along the normal to the burning surface. The burning zone is assumed to be stationary at  $x = 0$ ; that is, we think of the fresh gas as flowing with the velocity of  $v_n$  in the direction of the positive  $x$ -axis. Let the temperature of the fresh gas be  $T_0$ , that of the terminal gases  $T_c$ . As long as we use the concept of the ignition temperature, as is customary in the older works, we can assume that at a definite place in the burning zone this temperature  $T_z$  will be reached exactly and that the fresh gas to the left of it will be heated to  $T_z$  by conduction, while the gas at the right of it will be heated spontaneously by chemical reaction and will give off heat to the fresh gas by conduction. As long as we adhere to this conception, we can reason further: If  $c$  is the heat capacity of the fresh gas per  $\text{cm}^3$ , then the quantity of heat necessary to heat the  $v_n \text{ cm}^3$  of fresh gas that go through the burning surface per  $\text{cm}^2$  and second to the ignition temperature  $T_z$  is

$$\bar{c}v_n(T_z - T_0) \quad (37)$$

This quantity of heat is to be produced by conduction. It is reasonable to suppose that the temperature decrease at  $T_z$  is proportional to the

<sup>1</sup> MALLARD and LE CHATELIER, *Ann. mines*, (8), 4, 274 (1883).

difference  $T_e - T_z$ , so that the heat flow would be

$$k(T_e - T_z) \quad (38)$$

in which  $k$ , among other things, is proportional to the heat conductivity and inversely proportional to the distance in which the temperature rises from  $T_z$  to  $T_e$ . Equating (37) and (38) leads to

$$\bar{c}v_n(T_z - T_0) = k(T_e - T_z) \quad \text{or} \quad v_n = \frac{k(T_e - T_z)}{\bar{c}(T_z - T_0)} \quad (39)$$

This is the expression of Mallard and Le Chatelier. All elaborations of this theory of heat go beyond the original statement only in this respect, that they introduce the chemical reaction velocity in the region above  $T_z$  (and generally in a rather approximate and inadequate manner) and that the result is that the decrease in temperature is inversely proportional to  $v_n$ . In place of (38), we therefore get

$$k \frac{(T_e - T_z)}{v_n} \quad (38')$$

in which  $k$  is proportional to a reaction velocity factor as well as to conductivity. The combination of (37) and (38') results for  $v_n$  in

$$v_n = \sqrt{\frac{k}{\bar{c}} \frac{T_e - T_z}{T_z - T_0}} \quad (39')$$

The formulas of Crussard,<sup>1</sup> Daniell,<sup>2</sup> and Nusselt<sup>3</sup> can essentially be reduced to this form.<sup>4</sup>

We shall discuss Nusselt's formula in greater detail below and in connection with it discuss the possibilities and limits of the theory of heat. As questionable as it may be to introduce an ignition temperature in this connection, there will certainly be an average temperature below which the velocity of the chemical conversion can be disregarded. In the region in front of the burning zone, the heating of the fresh gas up to this temperature takes place exclusively by conduction. It is possible to treat accurately the conduction problem and the distribution of temperature in the fresh gas flowing into the burning surface if at a certain point the constant temperature  $T_z$  is maintained.<sup>5</sup> A tempera-

<sup>1</sup> CRUSSARD, L., *Compt. rend.*, **158**, 125, 340 (1914).

<sup>2</sup> DANIELL, P.J., *Proc. Roy. Soc. London, A*, **126**, 393 (1930).

<sup>3</sup> NUSSOLT, W., *Z. Ver. deut. Ing.*, **59**, 872 (1915). Cf. also JOUET, E., *Compt. rend.*, **156**, 872, 1058 (1913); **179**, 454 (1924). JOUGUET, E., and L. CRUSSARD, *Compt. rend.*, **168**, 820 (1919).

<sup>4</sup> For a critical discussion of the theory of heat, cf. also H.F. Coward and W. Payman, *Chem. Rev.*, **21**, 359 (1937).

<sup>5</sup> MICHELSON, "On the Normal Ignition Velocity of the Oxygen-hydrogen Mixture," Moscow, 1890. Cf. also MACHE, H., cited p. 70. In Mache, a numerical

ture distribution is obtained as it is indicated qualitatively in Fig. 85. Mache (cited page 70) has computed this temperature distribution numerically for a mixture of  $H_2$  and  $O_2$  with  $v_n = 130$  cm/sec and known temperature distribution. From this computation, we can reach an estimate of the "thickness" of the burning zone. If we compute the distance  $x$  beginning at a point at which the temperature begins to rise noticeably above  $T_0$  (for example, in Mache's computation, from  $T_0 = 273^\circ C$  it rose to 280 abs) to the point where  $T_z$  is reached, we get

$$\Delta x \cong 10^{-2} \text{ cm}$$

We shall therefore, in lieu of a better estimate, assume that the thickness of the burning zone lies in this range.

A simple derivation of the Nusselt formula for  $v_n$  can be found in Eucken.<sup>1</sup> First of all,  $Q$  represents the heat to be conducted to the fresh gas [Eq. (37)]

$$Q = \bar{c}v_n(T_z - T_0) \quad (40)$$

In place of (38), the formula for the heat flow at  $x_z$  (Figs. 84 and 85) is more generally written

$$Q' = \lambda \left( \frac{\partial T}{\partial x} \right)_{x=x_z} \quad (41)$$

(the decrease in temperature with positive sign appears here because we measure the heat flow in the direction of the negative  $x$ -axis).  $Q$  must again be equal to  $Q'$ . An expression for  $(\partial T/\partial x)_{x=x_z}$  must still be sought, however. With considerable simplification, it is assumed that the temperature rises linearly from  $T_z$ , that, in other words, when  $x = x_e$  the terminal temperature  $T_e$  is reached. In the same interval, the chemical conversion would therefore have to be completed; i.e., the concentration of the reaction products must have risen from  $\zeta = 0$  to  $\zeta = \zeta_e$ . The concentration decrease of the end products of reaction therefore becomes

$$\frac{\partial \zeta}{\partial x} = \frac{\zeta_e}{x_e - x_z} \quad (42)$$

For the decrease in temperature, which, according to Fig. 84, ought

---

value for  $k_0$  ten times too small is given in the table for which the heat conductivity is given at  $k_0 \sqrt{T}$ . The above values correspond to the column with heat conductivity proportional to  $T$  with corrected values.

<sup>1</sup> EUCKEN, A., Müller-Pouillet's "Lehrbuch der Physik," Vol. III/1, pp. 859ff., 1926.

to be  $\frac{\partial T}{\partial x} = \frac{T_e - T_z}{x_e - x_z}$ , we can also write

$$\frac{\partial T}{\partial x} = \frac{T_e - T_z}{x_e - x_z} = \frac{T_e - T_z}{\xi_e} \frac{\partial \xi}{\partial x} \quad (43)$$

i.e., the unknown distance ( $x_e = x_z$ ) is eliminated; it still remains, however, to express  $\partial \xi / \partial x$  by the reaction velocity. Again very much simplified, we assume the reaction velocity to be constant during the entire interval, to  $v_r$ , where  $v_r$  represents the increase in concentration of the end products in a unit of time,  $v_r = \partial \xi / \partial t$ . If we write

$$\frac{\partial \xi}{\partial x} = \frac{\partial \xi}{\partial t} \frac{dt}{dx} = \frac{v_r}{dx/dt} \quad (44)$$

in which  $dx/dt$  is apparently the velocity in which a particle moves in the  $x$ -direction, which we shall designate with  $v'_n$ , then

$$\frac{\partial T}{\partial x} = \frac{T_e - T_z}{\xi_e} \frac{v_r}{v'_n} \quad (45)$$

$v'_n$ , the flow velocity of an element at temperature  $T$  can be expressed by the flow velocity  $v_n$  at temperature  $T_0$

$$v'_n = \frac{T}{T_0} v_n \quad (46)$$

where it is assumed that the reaction takes place without change of the mol-number, or otherwise a factor taking this into account would have to be introduced. The latter, however, will be equal to 1 if we relate all magnitudes to  $T_z$  because no conversion has taken place there as yet, and therefore the same mol-number is still present as at the beginning. If we do this, we get

$$\left( \frac{\partial T}{\partial x} \right)_{x=x_z} = \frac{T_e - T_z}{\xi_e} \frac{(v_r)_z}{v_n} \frac{T_0}{T_z} \quad (47)$$

and, by insertion in (40),

$$v_n^2 = \frac{\lambda(T_e - T_z)T_0(v_r)_z}{\bar{c}(T_z - T_0)T_z\xi_e} \quad (48)$$

agreeing, essentially, with (39). It should be emphasized that all these simplifications are not entirely free from objection and particularly that they are not even strictly in agreement among themselves. Since, however, we shall later recognize the fundamental inadequacy of a pure theory of heat, we shall not discuss this in greater detail.

It is useful to recall that the general form of (48) is plausible and that several reasonable conclusions can be drawn from it. The combustion velocity according to (48) and likewise according to the original Mal-

lard-Le Chatelier formula (39) becomes greater as the maximum flame temperature increases above the ignition temperature  $T_0$ ; and it is smaller the higher  $T_z$  increases above the fresh gas temperature  $T_0$ . Further,  $v_n$  becomes greater, the greater the reaction velocity is in the burning zone, and the greater the conductivity  $\lambda$  becomes, and the smaller the heat capacity  $\bar{c}$  of the fresh gas becomes. All that is in agreement with what one would expect qualitatively. The formula also makes clear that the farther one moves from the stoichiometric composition in a fuel-air (or oxygen-air) mixture, toward the side of either air leanness or air excess, the more the liberated energy and therefore the maximum  $T_e$  must finally decrease. At the same time, however, the ignition temperature  $T_z$  can only rise; there must therefore be limits of mixture composition on both sides outside of which  $T_e - T_z$  is no longer positive and combustion can no longer propagate; *i.e.*, the theory of heat predicts the existence of ignition limits.

TABLE 15.—IGNITION LIMITS OF SEVERAL FUEL AND AIR, AS WELL AS FUEL AND OXYGEN MIXTURES (FROM TERRES)

| Gas                           | Ignition limits in    |                       |                       |                       |
|-------------------------------|-----------------------|-----------------------|-----------------------|-----------------------|
|                               | Air                   |                       | Oxygen                |                       |
|                               | Lower limit,<br>% gas | Upper limit,<br>% gas | Lower limit,<br>% gas | Upper limit,<br>% gas |
| H <sub>2</sub>                | 9.5                   | 65.2                  | 9.2                   | 91.6                  |
| CO                            | 15.6                  | 70.9                  | 16.7                  | 93.5                  |
| CH <sub>4</sub>               | 6.3                   | 11.9                  | 6.5                   | 51.9                  |
| C <sub>2</sub> H <sub>2</sub> | 4.2                   | 9.5                   | 4.1                   | 45.8                  |
| C <sub>2</sub> H <sub>4</sub> | 4.0                   | 14.0                  | 4.1                   | 61.8                  |
| C <sub>2</sub> H <sub>6</sub> | 3.5                   | 52.3                  | 3.5                   | 89.4                  |

At this point, a quantitative conclusion that is verified by experience can be drawn from the theory of heat. If, at the lower ignition limit of a fuel-air mixture (where the limit is effected by a lack of fuel), we imagine oxygen, which has approximately the same heat capacity as nitrogen, taking the place of atmospheric nitrogen, then nothing in (48) can change other than the factor of reaction velocity  $v_r$ .<sup>\*</sup> Since, however, as experience shows, the reaction velocity depends in general only slightly on the O<sub>2</sub> concentration, it can tentatively be assumed that (48) remains unchanged. The result of this would be that the lower ignition limit in mixtures with air and with oxygen would have to be approximately the same. That this is actually the case is shown by Table 15, in which

<sup>\*</sup> And perhaps the influence of diffusion of O<sub>2</sub>-molecules.

lower and upper ignition limits for several substances in mixture with air (according to Terres) are given.<sup>1</sup> It is further shown by Table 16 in which numerical values have been taken from a later compilation by Lewis and v. Elbe.<sup>2</sup>

TABLE 16.—IGNITION LIMITS, LOWER LIMITS IN AIR OR OXYGEN (FROM LEWIS AND v. ELBE)

| Material                               | C <sub>3</sub> H <sub>6</sub> | Ethyl ether | Divinyl ether | Cyclopropane |
|--|-------------------------------|-------------|---------------|--------------|
| Lower limit in air, %.....             | 2.00                          | 1.85        | 1.70          | 2.40         |
| Lower limit in O <sub>2</sub> , %..... | 2.10                          | 2.10        | 1.85          | 2.45         |

The compilations show that actually the lower ignition limits in air and oxygen mixtures generally lie remarkably close together.

A further conclusion from (48) supported by experience is the influencing of the combustion velocity by substituting for an inert gas a similar one with the same conductivity but different heat capacity. Then the inert gas with higher heat capacity ( $\bar{c}$ ) must reduce the combustion velocity. If, for example, in methane-air mixtures, CO<sub>2</sub> is substituted for nitrogen, the combustion velocity is reduced by about one-half and the ignition limits are narrowed. This has important practical applications for the prevention of explosions.<sup>3</sup> If, conversely, argon is substituted for nitrogen, the combustion velocity rises to several times its original value.<sup>4</sup> The heat conductivity at 0°C for A, CO<sub>2</sub>, and N<sub>2</sub> are, respectively, 3.8, 3.3, and  $5.7 \cdot 10^{-5}$ . Only argon and carbonic acid are directly comparable, since their conductivity does not differ much. The essentially higher combustion velocity of argon as opposed to carbonic acid must therefore be due principally to the smaller heat capacity and therefore higher flame temperature in the argon mixture. If mixtures in which at one time helium and at another time argon is the inert gas, both of which have the same heat capacity, are now compared, the combustion velocity should show only a difference in the heat conductivity. Coward and his associates especially have emphasized the crucial nature of this experiment for any theory of heat. In Fig. 86, taken from Coward and Jones,<sup>5</sup> flame velocities of methane and air mixtures are given, in which the atmospheric nitrogen was replaced by helium or argon. To be sure, the increase in flame velocity for the rarer gases on account of their higher flame temperatures is noticeable, but the considerable increase to be expected according to the theory

<sup>1</sup> TERRES, *Gas- u. Wasserfach*, **63**, 785, 805, 820, 836 (1920).

<sup>2</sup> LEWIS, B., and G. v. ELBE, *Chem. Rev.*, **21**, 347 (1937).

<sup>3</sup> For numerical values, see G. Jahn, Karlsruhe dissertation, 1934.

<sup>4</sup> COWARD and HARTWELL, cited p. 97.

<sup>5</sup> COWARD, H.F., and G.W. JONES, *J. Am. Chem. Soc.*, **49** (1927).



of heat does not materialize. The conductivity of pure helium is about eight times greater than that of argon. The flame velocity with helium is, however, only about 15 per cent higher than that with argon. Coward and Payman (cited page 107) report more recent experiments according to which, for hydrogen mixtures with "atmospheres" of

$$\left( 21 \text{ per cent O}_2 + 79 \text{ per cent } \begin{pmatrix} \text{He} \\ \text{Ne} \\ \Lambda \end{pmatrix} \right),$$

systematic differences among the various rare gases are hardly perceptible. We reproduce Table 17 from the same work, with more recent values for

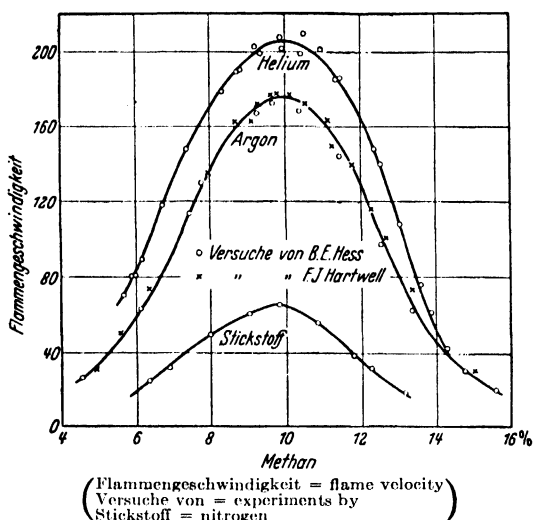


FIG. 86.—Flame velocities of methane in atmospheres of  $\text{O}_2\text{-N}_2$ ,  $\text{O}_2\text{-He}$  and  $\text{O}_2\text{-A}$ . [From Coward and Jones, *J. Amer. Chem. Soc.*, vol. 49 (1927).]

flame velocities and the normal combustion velocities of methane in mixture with nine times the amount of an "atmosphere," in which helium is present at one time and argon at another instead of nitrogen. Unfortunately, no data on the heat conductivity are given for the gas mixtures in question, and for that reason it is difficult to say with certainty in the latter case, where the relation of the combustion velocities in He- and A-atmospheres is about 1.4, whether this is less than the ratio of the roots from the conductivities. (Application of the mixing rule by using the conductivities determined at  $0^\circ\text{C}$  would yield a value almost twice as great; however, the conductivity can vary considerably from that computed according to the mixing rule. In addition, the conductivity for higher temperatures would have to be taken, and it is uncertain which temperature comes into consideration in this case.)

At any rate, it suffices that there are cases in which relations appear which are not at all predictable by the theory of heat. It will therefore be necessary to accept the conclusion of Coward and his associates that at least in its pure form the theory of heat alone does not suffice to describe the observable facts.

TABLE 17.—FLAME VELOCITIES IN A TUBE 2.5 CM IN DIAMETER FOR MIXTURES OF 1 METHANE AND 9 PARTS OF THE FOLLOWING ATMOSPHERES (FROM COWARD AND PAYMAN)

| Atmosphere                       | Velocity of the uniform flame movement, cm/sec | Flame surface, cm <sup>2</sup> | Normal combustion velocity, cm/sec |
|----------------------------------|--|--------------------------------|------------------------------------|
| 20.9O <sub>2</sub> + 79.1He..... | 206  | 12.3                           | 82                                 |
| 20.9O <sub>2</sub> + 79.1A.....  | 138  | 11.4                           | 59                                 |

A pure thermal theory of combustion is, however, to be rejected at the outset for theoretical considerations in general. First of all, the theory of heat in its above form (disregarding entirely the simplifications made in applying it) must be objected to because the concept of an "ignition temperature" is inadequate.<sup>1</sup> The effect of this concept on the results is, among other things, that, from the formulas given above with a generally accepted value for  $T_z$ , too great a dependence of the combustion velocity on temperature would result. This dependence would have to become infinite for  $T_0 = T_z$ , whereas in reality  $v_n$  still maintains finite values at temperatures far above the usual "ignition temperatures."<sup>2</sup> That the temperature dependence of  $v_n$  is rather small was shown, for example, by Ubbelohde<sup>3</sup> as well as Sachsse. It is well to recognize what is understood by ignition temperature: It is that temperature at which a given mixture of gas under a given condition (generally enclosed in a container) ignites after a definite induction time. It is essential that this apply to a process in which a larger mass of gas, left to itself, explodes after the lapse of some time. Let us now follow a thin layer of gas on its path through a burning zone.<sup>4</sup> Let the thickness of the layer be so small that the temperature can be regarded as uniform (*i.e.*, a thickness of probably  $\ll 10^{-2}$  cm); it will then be seen that the conditions in it are not at all comparable with those of auto-ignition. In the first place, auto-ignition temperatures are customarily

<sup>1</sup> Cf. the supplement to Chap. I.

<sup>2</sup> For further material on this, in itself a well-known fact, see also H. Sachsse, *Z. physik. Chem.*, Sec. A, **180**, 305 (1937).

<sup>3</sup> UBBELOHDE, L., and M. HOFSSÄSS, *Gas- u. Wasserfach*, **56**, 1225, 1252 (1913).  
 UBBELOHDE, L., and O. DOMMER, *Gas- u. Wasserfach*, **57**, 733, 757, 781, 805 (1914).

<sup>4</sup> Cf. JOST, W., and L. v. MÜFFLING, *Z. physik. Chem.*, Sec. A, **181**, 208 (1938).

determined at induction periods that are much too long to come into consideration for the flame. Sachsse especially pointed out this fact. Then, while the thin layer takes its course through the burning zone, a constant equalization of temperature takes place by means of conduction and the balance of material by diffusion with neighboring layers. Thus the temperature and composition of the layer must constantly change. Hence the reaction velocity within the burning zone must likewise constantly change. It cannot be equal to zero under  $T_z$  and jump to a finite, large value at  $T_z$ .

One could object to this that, by the existence of ignition temperatures (limits of explosion), the possibility (in a physical sense) of an irregular change of the reaction velocity with the temperature is proved. This, however, is not true. Even where explosion limits appear, the reaction velocity constantly changes with the temperature. To make this clear, let us look at Fig. 87. In it, the reaction velocity  $v_r$  is given as a function of the time  $t$ , and it is given for two different initial temperatures which lie a little above and below the ignition temperature.

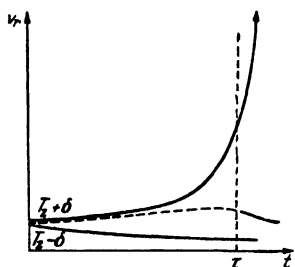


FIG. 87.—Reaction velocity as a function of the time for temperatures a little above or below the "ignition temperature."

The change in time of  $v_r$  is much different, however. Below  $T_z$ , there is a gradual decline of  $v_r$  in time (sometimes it rises at first and then declines; see the dotted line). Above  $T_z$ ,  $v_r$  rises at first slowly, then faster and faster with time until it trends toward a very great value at the end of the induction period  $\tau$ . What one usually does is to compare the reaction velocities at  $t = \tau$ . These are extremely different for initial temperatures above and below  $T_z$ . But above  $T_z$ ,  $v_r$  can have risen for only two reasons, either because in the course of conversion the temperature has risen (thermal explosion), but then at the time  $t = \tau$  the two samples do not have at all similar temperatures; hence a great difference in the reaction velocity does not mean irregular change with the temperature. On the other hand, the concentration of the active particles has risen extremely during the induction period by means of chain-branching. But then the comparison of the reaction velocities at  $t = \tau$  means that one is comparing not neighboring conditions but rather some with considerable differences, this time in the concentrations. Here too, therefore, the apparently irregular change of velocity is only the result of a finite difference in a different entity. Hence the reaction velocity changes under all circumstances regularly with temperature and concentration (insofar as one actually considers all con-

centrations, even those of active particles). Since, as we have seen, none of these entities can change irregularly in layers bordering on the burning zone, the reaction velocity cannot change either. As a result, the introduction of an ignition temperature in the treatment of the burning zone is not justified.

It is already clear from a qualitative point of view that diffusion too plays a role. The following consideration, which is to serve only as a rough estimate, shows that the influence of diffusion, like that of conduction, is never to be neglected. If  $\lambda$  is the conductivity of a gas mixture, the formulas of the elementary kinetic gas theory show that approximately

$$\lambda \cong D\bar{c} \quad (49)$$

if  $D$  is the coefficient of diffusion (really the coefficient of self-diffusion) and  $\bar{c}$  the heat capacity per  $\text{cm}^3$ ; therefore

$$\bar{c} = \bar{c}_s \zeta \quad (50)$$

where  $\bar{c}_s$  is the average specific heat and  $\zeta$  is the total concentration of all components of the gas. Let us observe a simplified picture of the burning zone (Fig. 88), and let us assume the concentration of the reacting material or materials to be  $\zeta_0$  at the beginning and 0 at the end, and let the burning zone have the thickness  $\Delta x$  (which of course is not very exactly defined); then, for the heat flow in the direction of the negative  $x$ -axis we get,

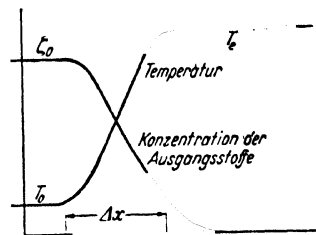
$$w_x \cong +\bar{\lambda} \frac{\partial T}{\partial x} \cong +\bar{D}\bar{c} \frac{T_s - T_0}{\Delta x} \quad (51)$$

in which use has been made of the relations above, and an average drop in temperature has been inserted. For the diffusion current, *i.e.*, the amount of material diffused into the burning zone in a unit of time from the fresh gas per  $\text{cm}^2$  of cross section, we get

$$s_x \cong +\bar{D} \frac{\zeta_0}{\Delta x} \quad (52)$$

with the same approximations as above.

Since it is a matter of two different entities when dealing with the diffusion current and the thermal current, a comparison is possible only on the following basis: The thermal current shows how many calories per second and per  $\text{cm}^2$  flow from the burning zone into the fresh gas. Obviously only the heating value conducted by the diffusion current of



(Konzentration der Ausgangsstoffe = concentration of the initial materials)

FIG. 88.—Distribution of the temperature and the concentration of the initial materials ( $\zeta$ ) in the burning zone.

the fresh gas is comparable to it; *i.e.*, if  $Q$  is the heat of reaction per mol

$$s_x Q \cong \bar{D} \frac{\xi_0}{\Delta x} Q \quad (53)$$

On the other hand, the temperature  $T_e$  is reached when complete conversion takes place; thus heat capacity times  $(T_e - T_0)$  must be equal to the heat of reaction; in other words

$$\bar{c}_p(T_e - T_0) = Q \quad T_e - T_0 = \frac{Q}{\bar{c}_p} = \frac{Q}{\bar{c}} \xi \quad (54)$$

in which use is made of (50).<sup>1</sup>

Hence the heat flow becomes

$$w_x \cong \bar{D} \bar{c} \frac{Q}{\Delta x} \xi \cong \frac{\bar{D} Q \xi}{\Delta x} \quad (55)$$

If we disregard the differences between the average values designated by the bars as compared with corresponding magnitudes at a given temperature, the heat flow in one direction is identical with the flow of available reaction energy transported in the opposite direction. These computations represent only very rough approximations, but we are concerned only with showing that the two magnitudes are of the same order and that we must not neglect diffusion or heat conduction.

One could also imagine as a borderline case (which of course would do just as little justice to the actual situation as would a one-sided theory of heat) the following process of flame propagation: The fresh gas in front of the burning surface diffuses constantly into the hot burning zone where it reacts practically instantaneously. The diffusion process would be determining for the velocity. It is of interest that it would not be difficult to understand combustion velocities of the order of magnitude up to 1 m/sec in this manner (Jost and v. Muffling, cited page 113).

The hitherto considered influence of the diffusion of the fresh gas and the terminal gas as a whole might, however, in general not even be so important as the diffusion of active particles which can be present in considerable concentration in the thermal equilibrium, and which in the burning zone can even exceed this equilibrium concentration as the result of chain-branching (*cf.* Chap. VIII). The concentration of free atoms and radicals can be calculated entirely according to the percentages of the total gas (*cf.* the extreme example of the detonation of an oxygen-hydrogen mixture, Chap. V, page 174). Since the free atoms and radicals are very active, a relatively small current of these particles is equivalent to a considerable flow of energy. More important, however, is the following: Only a small portion of the heat conducted serves as

<sup>1</sup> And the difference between  $c_p$  and  $c_v$  is neglected. This is allowable in this rough approximation.

"heat of activation" of reacting particles (*cf.* in this connection Chap. VIII). However, the energy of free atoms and radicals is used to a certain extent completely as activating energy. One can again estimate (*cf.* Jost and v. Muffling, cited page 113) that many more than ten times the active particles can get to the colder layers of the burning zone by diffusion than would be there in equilibrium.

How a strictly theoretical treatment of the normal combustion velocity is to be attacked is thus clear. Conduction must be considered, but diffusion is also to be taken into account, and diffusion of all the kinds of particles appearing, inclusive of short-lived intermediary; finally the reaction velocity as a function of the temperature and of the composition is to be introduced explicitly. The inadequate concept of ignition temperature is to be avoided.

Let us again imagine the burning surface in our system of reference as being stationary; *i.e.*, if, as in Fig. 88, page 115, we let the fresh gas flow with the velocity  $v_n$  in the direction of the positive  $x$ -axis, all the entities within the burning zone in this system of references must be stationary. An equation of the following form must therefore apply at each place of the burning surface for the temperature as well as for the concentration of each individual material component, inclusive of the active intermediate products

$$\begin{aligned}\frac{dT}{dt} &= 0 \\ \frac{dc_i}{dt} &= 0 \quad i = 1, 2, 3, \dots\end{aligned}\quad (56)$$

where  $c_i$  is the concentration of the material component  $i$ . The entire change with time of one of these entities is composed of (1) the "conduction" action (heat conduction in the case of the heat energy, diffusion in the case of the individual concentration), (2) the convective action, the action of flow, and (3) change as the result of chemical reaction. The heat flow in the  $+x$ -direction is, for example,

$$w_x = -\lambda \frac{\partial T}{\partial x}$$

a quantity of heat flows at the point  $x$  in a unit of time into a volume element of the thickness  $\Delta x$  and of  $1 \text{ cm}^2$  cross section

$$(I) \quad w_x = -\left(\lambda \frac{\partial T}{\partial x}\right)_x$$

at the point  $x + \Delta x$  the quantity of heat that flows out is

$$(II) \quad w_{x+\Delta x} = -\left(\lambda \frac{\partial T}{\partial x}\right)_{x+\Delta x} \cong -\left(\lambda \frac{\partial T}{\partial x}\right)_x - \Delta x \frac{\partial}{\partial x} \left(\lambda \frac{\partial T}{\partial x}\right)_x$$

The excess of the heat flowing in over that flowing out is therefore

$$(I) - (II) = \Delta x \frac{\partial}{\partial x} \left(\lambda \frac{\partial T}{\partial x}\right) \quad (57)$$

Since the volume of the layer of the cross section amounts to  $(1 \text{ cm}^2 \Delta x) \text{ cm}^3$ , the

change of the heat content by conduction of the unit of volume becomes

$$\left(\frac{\partial W}{\partial t}\right)_{\text{cond}} = \frac{\partial}{\partial x} \left( \lambda \frac{\partial T}{\partial x} \right) \quad (58)$$

Since  $\lambda$  varies with the temperature and the location, it must appear behind the differentiation symbol. For the change in concentration of the material components  $i$  by diffusion, one obtains by analogy

$$\left(\frac{\partial c_i}{\partial t}\right)_{\text{diff}} = \frac{\partial}{\partial x} \left( D_i \frac{\partial c_i}{\partial x} \right) \quad (59)$$

By convection, the quantity of heat that flows through a cross section of 1 cm<sup>2</sup> is

$$\bar{c}_p \rho T v \quad (60)$$

where  $\bar{c}_p$  is the average specific heat per gram between 0 and  $T$  deg,  $\rho$  the density,  $T$  the temperature, and  $v$  the velocity of flow (which is likewise dependent on  $x$  on account of the change of volume with  $T$  and  $x$ ). As above, one obtains the resulting change of the heat content with time

$$\left(\frac{\partial W}{\partial t}\right)_{\text{flow}} = - \frac{\partial}{\partial x} (\bar{c}_p \rho T v) \quad (61)$$

For the corresponding changes of concentration, the following is valid:

$$\left(\frac{\partial c_i}{\partial t}\right)_{\text{flow}} = - \frac{\partial}{\partial x} (c_i v) \quad (62)$$

As a change by means of reaction velocity, we obtain, if we designate the reaction velocity with  $U$  (let  $U$  be the change in concentration in a unit of time, hence of the dimension mol/cm<sup>3</sup> sec), and if with  $\nu_i$  we designate the number of mols of the substance  $i$  which disappear in a conversion corresponding to the reaction equation<sup>1</sup> for the concentration of the substance  $i$

$$\left(\frac{\partial c_i}{\partial t}\right)_{\text{react}} = - \nu_i U \quad (63)$$

If  $Q$  is the heat of reaction, for the heat content we obtain correspondingly

$$\left(\frac{\partial W}{\partial t}\right)_{\text{react}} = QU \quad (64)$$

For the total change of the individual entities that must be present in the stationary burning zone 0, we thus obtain

$$\frac{dW}{dt} = \frac{\partial}{\partial x} \left( \lambda \frac{\partial T}{\partial x} \right) - \frac{\partial}{\partial x} (\bar{c}_p \rho T v) + QU = 0 \quad (65)$$

$$\frac{dc_i}{dt} = \frac{\partial}{\partial x} \left( D_i \frac{\partial c_i}{\partial x} \right) - \frac{\partial}{\partial x} (c_i v) - \nu_i U = 0 \quad (66)$$

By dividing Eq. (65) with  $\rho \bar{c}_p$ , we arrive at the equation  $dT/dt = 0$ , and (65) is therefore equivalent to the latter. In addition, there are relations that follow from the reaction equation, such as the hydrodynamic continuity equation for the conservation

<sup>1</sup> For the designations used as well as the derivation of the formulas, see G. Damköhler, "Der Chemieingenieur," Vol. III, 1. We have followed Damköhler here.

of mass

$$\frac{\partial}{\partial x}(\rho v) = 0 \quad (67)$$

which simply says that the same quantity of substance flows through each cross section. In principle, it is possible to compute the combustion velocity from these equations. One needs for this purpose the conductivity of the mixture as well as the diffusion coefficients of the individual components, all of them dependent on the temperature, which can be computed fairly accurately from kinetic gas data. Further, one would need to know the reaction velocities, and it is here that the chief difficulty arises; for up to this time it is difficult to say anything valid about the reaction velocity under the extreme conditions of the flames. The need is rather to proceed in the opposite direction and to obtain the reaction velocities from the flame velocities. Even if the reaction velocities were known, computing the normal combustion velocities with the aid of the above equations would be no easy task, but it would be possible in principle by numerical integrations.

Lewis and v. Elbe<sup>1</sup> have sought to simplify the problem in the following manner: We have seen in the rough estimate made on page 116, in order to compare heat conduction and diffusion, that the energy transported in one direction by conduction is always of the same order of magnitude as the chemical energy that the diffusing fresh gas takes with it in the opposite direction. If this average relation, valid for the entire burning zone, is assumed to be exactly fulfilled at every single place, and if the energy transported by active particles is disregarded, the conduction equation could be left out of consideration and satisfied indirectly by introducing the condition that the entire energy, *i.e.*, the sum of chemical energy and heat energy, must be constant over the burning zone. This is an assumption that is certainly not fulfilled exactly but represents a reasonable simplification for purposes of approximation. By means of this simplification, Lewis and v. Elbe have succeeded in completing an absolute computation of the normal combustion velocity in the case of a simple example, namely, ozone explosion.

With considerable probability, a simple reaction mechanism can be assumed here.



in which fairly accurate values for the equilibrium 1 and the velocity 2 are available.

For details of the rather lengthy calculation, which includes several items that must be disregarded, we refer to the original work as well as to the monograph by Lewis and v. Elbe. Information as to the degree of exactness achieved can be obtained from Table 18.

<sup>1</sup> LEWIS, B., and G. v. ELBE, *J. Chem. Phys.*, **2**, 537 (1934); *cf.* also the same, "Combustion, Flames and Explosions of Gases"; further, *Chem. Rev.*, **21**, 347 (1937).



TABLE 18.—NORMAL COMBUSTION VELOCITY OF OZONE AND OXYGEN MIXTURES. COMPUTED AND OBSERVED VALUES BY LEWIS AND v. ELBE

| $p$ , mm Hg | $T_0^\circ$ abs | $T_e^\circ$ abs | $m^*$ | $(v_n)$ observed, cm/sec | $(v_n)$ computed, cm/sec |
|-------------|-----------------|-----------------|-------|--------------------------|--------------------------|
| 624         | 300             | 1239            | 3.05  | 55                       | 253                      |
| 2560        | 427             | 1343            | 3.05  | 158                      | 451                      |
| 495         | 302             | 1922            | 1.02  | 160                      | 333                      |
| 3760        | 468             | 2044            | 1.02  | 747                      | 664                      |

The agreement between theory and experiment is remarkably good considering the many factors that go to make up the result. At any rate, it could not be expected to be any better, for it is a matter of an actual absolute calculation of the velocity. Of interest is Fig. 89 by Lewis and v. Elbe, in which the structure of the flame front is worked out for a

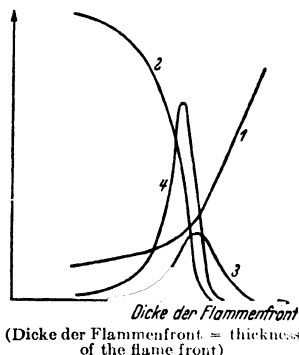


FIG. 89.—Structure of the burning zone in ozone explosions. [From Lewis and v. Elbe, *J. Chem. Phys.*, vol. 2 (1934).] 1 =  $T$ . 2 =  $[O_3]$ . 3 =  $[O]$ . 4 = reaction velocity.

particular example. The thickness of the flame front is given as  $\sim 10^{-3}$  cm, which is probably somewhat too small. At least the heat flow, which is figured from the maximum temperature decrease in the figure, is unreasonably high. If we assume that the burning zone is twice as thick as Lewis and v. Elbe have computed—and this lies well within the limits of error of their computation—and if we suppose it to be inversely proportional to the pressure, we should obtain values for atmospheric pressure that would approximate those estimated by Maché. The concentration of ozone constantly falls off over the burning zone; correspondingly the concentration of the oxygen, which is not given, must increase.

The concentration of O-atoms, as well as the reaction velocity, has a definite maximum within the burning zone.

In general, it may be said of the calculation of Lewis and v. Elbe that it still contains a number of disregarded factors that we should like to have worked out (the improbable course of the temperature, for example, is due to this, with irregular change of the differential quotients  $T = T_e$ ) but that it represents by far the most reasonable solution thus far offered for computing the combustion velocity. For further discussion, we refer to Lewis and v. Elbe (cited page 119) as well as to Jost and v. Müffling (cited page 113).

**7. Reaction Velocity and Normal Velocity of Combustion.**—That reaction velocity is of decisive importance for flame propagation is

clear from all the attempts to treat it theoretically, even though it is impossible by the nature of things to give an explicit relation between flame velocity and reaction velocity. Observations that point to such influences have been made again and again in the course of investigations. Ubbelohde and Dommer<sup>1</sup> found, for example, that the combustion velocity of carbon monoxide and air mixtures of maximum velocity<sup>2</sup> rises from 16 cm/sec for dry gases to about 55 cm/sec for gases with 9.4 per cent H<sub>2</sub>O. Here the same reaction-accelerating influence of vapor is observable as in slow oxidation and also in detonation (Chap. V). This vapor influence can also be seen in flame velocity, as is shown in Table 19, taken from Bone.

TABLE 19.—FLAME VELOCITY OF A MIXTURE OF 45 PER CENT CO IN AIR, WITH VARYING H<sub>2</sub>O CONTENT IN A TUBE 2.5 CM IN DIAMETER

| % H <sub>2</sub> O          | 0.70 | 1.45 | 3.50 | 5.20 | 8.00 |
|-----------------------------|------|------|------|------|------|
| Flame velocity, cm/sec..... | 56   | 76   | 106  | 120  | 118  |

Systematic investigations on reaction velocity and flame velocity have been made especially by Bunte<sup>3</sup> and his associates. We shall discuss these briefly here. The combustion velocity of carbon monoxide is accelerated not only by vapor but also by hydrogen, as well as by organic compounds containing hydrogen, a sign that OH-radicals and perhaps also H-atoms probably participate in the reaction.<sup>4</sup> Their presence would in itself accelerate the reaction, but they can also increase the combustion velocity indirectly by diffusing especially rapidly. It is noteworthy also that materials whose combustion velocities are somewhat lower than that of the (somewhat damp) carbon monoxide can considerably raise the combustion velocity of the latter when mixed with it in small quantities. For example, 1 per cent of hexane (whose maximum combustion velocity, 32 cm/sec, is much lower than that of the related damp carbon monoxide with 42 cm/sec) raises the combustion velocity of carbon monoxide by 29.5 per cent. The deviation of the combustion velocities of mixtures of maximum velocity consisting of carbon monoxide with a number of added gases from the values computed according to the rule of mixtures can be found in Hartmann. It is

<sup>1</sup> UBBELOHDE, L., and O. DOMMER, *Gas- u. Wasserfach*, **57**, 733, 757, 781, 805 (1914).

<sup>2</sup> Maximum velocity in respect to the variation of the fuel-air relation.

<sup>3</sup> BUNTE, K., *Gas- u. Wasserfach*, **75**, 213 (1932). BUNTE, K., and associates, *Gas- u. Wasserfach*, **73**, 837, 871, 890 (1930); **74**, 1073 (1931); **76**, 89 (1933); further, the Karlsruhe dissertations of G. Jahn (1934), E. Hartmann (1931), and G. Seuffert (1934).

<sup>4</sup> Cf. Chap. IX.

uniformly demonstrated that small mixtures of compounds containing hydrogen raise the combustion velocity far above the value deduced from the mixing rule. Carbon disulphide has the opposite effect.

TABLE 20.—INFLUENCING THE NORMAL COMBUSTION VELOCITY BY IRON CARBONYL ADDITIONS. COMPOSITION OF THE MIXTURE CORRESPONDS TO THE MIXTURE OF MAXIMUM COMBUSTION VELOCITY (FROM HARTMANN)

| Mixture with air           | $(v_n)_{\max}$     |  |
|----------------------------|--------------------|--|
|                            | Without,<br>cm/sec | With addition<br>of $\text{Fe}(\text{CO})_5$ ,<br>cm/sec |
| Ethyl ether.....           | 37.5               | 34.8   |
| 90% CO + 10% ether.....    | 51.5               | 49.5   |
| 97.5% CO + 2.5% ether..... | 61.5               | 58.5   |

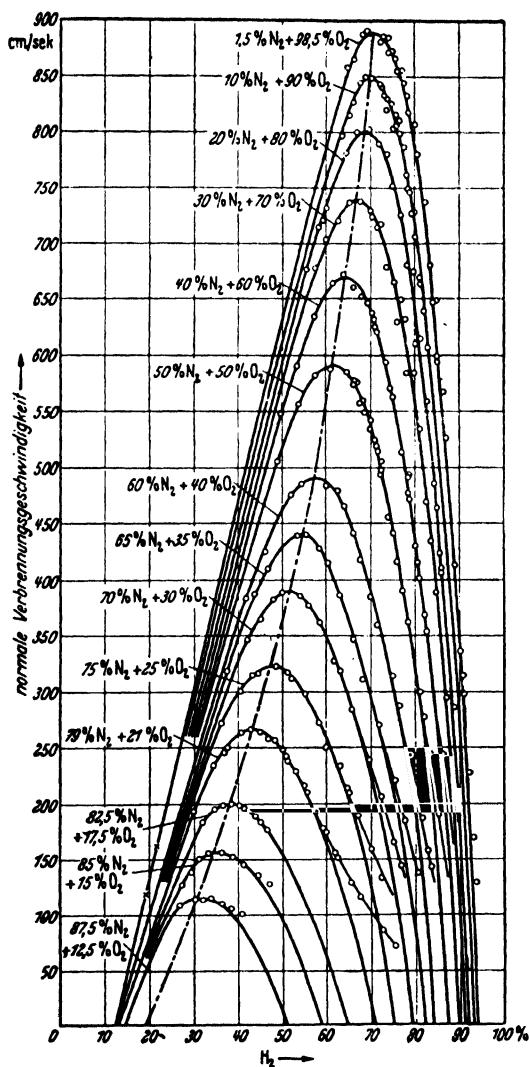
It might be supposed that the addition of antiknock products would especially decrease the combustion velocity. The experiments show a certain inhibiting effect, but this is not great by any means. In Table 20 are given values on the decrease of combustion velocities in mixtures of maximum velocities consisting of ethyl ether, as well as ethyl ether + carbon monoxide with air by the addition of iron pentacarbonyl [1 cm<sup>3</sup> of liquid  $\text{Fe}(\text{CO})_5$  to 100 cm<sup>3</sup> of ethyl ether], according to Hartmann.

TABLE 21.—MAXIMUM COMBUSTION VELOCITIES OF VARIOUS MATERIALS IN MIXTURE WITH AIR (FROM E. HARTMANN'S COMPILATION)

| Fuel  | $(v_n)_{\max}$ ,<br>cm/sec | Mixture,<br>% gas in<br>air | Stoichiometric<br>mixture, % gas<br>in air |
|---|----------------------------|-----------------------------|--|
| Hydrogen.....                                     | 267                        | 42                          | 29.5                                       |
| Acetylene.....                                    | 131                        | 10                          | 7.7  |
| Ethylene.....                                     | 63                         | 7.0                         | 6.5  |
| Carbon disulphide.....                            | 48.5                       | 8.2                         | 6.5  |
| Propylene.....                                    | 43.5                       | 4.8                         | 4.5  |
| Carbon monoxide + 1.2% $\text{H}_2\text{O}$ ..... | 41.5                       | 53                          | 29.5                                       |
| Benzol + 0.5% $\text{H}_2$ .....                  | 38.5                       | 3.0                         | 2.7  |
| Ethyl ether.....                                  | 37.5                       | 4.5                         | 3.4  |
| Methane.....                                      | 37.0                       | 10.5                        | 9.5  |
| Cyclohexane.....                                  | 35.0                       | 2.5                         | 2.3  |
| n-Pentane.....                                    | 35.0                       | 2.9                         | 2.6  |
| n-Hexane.....                                     | 32.0                       | 2.5                         | 2.2  |
| Acetone.....                                      | 31.8                       | 6.0                         | 5.0  |

Probably there is a decrease of  $v_n$  by the addition of considerable  $\text{Fe}(\text{CO})_5$ , but it remains relatively unimportant.

We have already pointed out that the mixtures of maximum velocity always lie on the side of excess fuel. In Table 21, which is likewise from Hartmann, we present a compilation that illustrates this fact.



(normale Verbrennungsgeschwindigkeit = normal combustion velocity)

FIG. 90.—Normal combustion velocities of  $H_2$  in mixture with various "atmospheres" of  $N_2 + O_2$ . [From Jahn, Karlsruhe Dissertation (1934).]

The reason for this may be, in part, the factor of reaction velocity; for, since the reaction velocity in by far the most cases depends much more on the fuel concentration than it does on the oxygen concentration,

its maximum will be on the side of fuel excess. An added factor might be the fact that, in substances containing hydrogen, an excess of fuel has a favorable effect on the formation of free hydrogen as well as hydrogen atoms as its reaction product, and this might be favorable to the propagation of the combustion by diffusion of the especially active free H-atoms.

Jahn (cited page 123) discusses extensive experimental material in respect to Nusselt's formula for combustion velocity. Even though we might consider it merely of historical interest, the results are nevertheless of more general importance.

The combustion velocities of mixtures with different "atmospheres" have also been measured by Jahn. In order to illustrate the relations, we reproduce in Fig. 90 combustion velocities of hydrogen in various  $N_2$ - $O_2$  atmospheres. Jahn (cited page 123) also gives groups of curves for  $CO_2$ - $O_2$  atmospheres. In the various  $N_2$ - $O_2$  atmospheres, the conductivity, diffusion coefficient, heat capacity, and hence also (at least in the range of fuel deficiency) the maximum flame temperature remain approximately unchanged. The differences in combustion velocity must therefore be due to differences in the reaction velocity and in the varying concentration (but not the mobility) of active particles. In the case of the  $CO_2$ - $O_2$  atmospheres, the heat capacity is changed, and the effect is noticeable in  $v_n$ . In addition, the change in conductivity and in the diffusion coefficients plays a role. Unfortunately, it is not yet possible to draw conclusions as to the reaction velocity from these investigations. In the work of Jahn, there are experiments similar to those above with CO and  $CH_4$  as fuel gas.

**8. Limits of Ignition.**—The appearance of ignition limits is conditioned by the fact that, outside of certain limits of composition, a combustion locally induced by extremely powerful means is no longer able to propagate. The limits of combustion thus appear where the propagation velocity for explosion has become zero. To be sure, it is not said that the limit obtained from measured values of the combustion velocity by extrapolation to a zero combustion velocity must be the exact ignition limit; for the smaller the combustion velocity, the more will disturbances by conduction, etc., make themselves felt, and the more will the ignition limits depend on external factors like the diameter of the container. That is probably why it is generally not successful to observe combustion velocities under a certain limit, frequently in the neighborhood of  $\sim 10 - 20$  cm/sec.

It is convenient to have at one's command at least a semiquantitative estimate for heat conduction to the wall in the case of flame propagation in a tube. Since the formal theory of heat conduction is identical with that of diffusion, one can, for purposes of orientation, give the formula

$$\overline{\Delta x^2} = 2Dt \quad (68)$$

which is analogous to the expression for the average square of displacement of a particle

$$\overline{\Delta x^2} = 2kt \quad (69)$$

In (69),  $k$  is the thermometric conductivity (diffusivity), not the heat conductivity  $\lambda$ , for  $k = \lambda/\bar{c}$ , if  $\bar{c}$  is the average specific heat per  $\text{cm}^3$ .  $\sqrt{\Delta x^2}$  in order of magnitude would be approximately the distance from the wall at which the temperature of a hot gas (temperature  $T_1$ ) that has been brought in contact with a cold wall of the constant temperature  $T_0$  has fallen to about  $(T_0 - T_1)2$ . For practical application, it should be remembered that  $k$  varies considerably with the temperature but that the formulas above are valid assuming  $k$  to be constant. An average value will thus be assumed for  $k$ , taken according to the temperature interval considered. For hot burning gases,  $k$  will at any rate not be smaller than  $1 \text{ cm}^2/\text{sec}$ . For  $t$ , a time will be taken that is of the same order of magnitude as the time during which the burning zone passes a point on the wall. In other words, if  $\delta$  is the thickness of the burning zone and  $v_f$  the flame velocity,

$$t \sim \frac{\delta}{v_f}$$

With  $\delta \cong 10^{-2} \text{ cm}$  and  $v_f = 20 \text{ cm/sec}$  (we are taking a low value for  $v_f$  because at low flame velocities in the neighborhood of the ignition limits the influence of the wall is strongest and interests us especially), we get

$$t \cong 5 \cdot 10^{-4} \text{ sec}$$

and thus

$$\sqrt{\Delta x^2} \cong \sqrt{10^{-3}} \cong 0.3 \text{ mm}$$

thus the thickness of the layer in which the cooling from the wall makes itself strongly felt will be of this order of magnitude. From this, by the way, it can also be seen, as has already been mentioned (page 102) as an experimental result, that the material of the wall is practically without influence. Because the heat capacity of the wall material is about 1000 times greater than that of the gas at atmospheric pressure, the rise in temperature of the wall at an equal depth of penetration would amount to only  $1/1000$  of the cooling of the gas. This means, however, that one may, as a first approximation, regard the temperature of the wall, whatever its composition, as being constant during the progress of the flame front.

The following estimate is somewhat more exact and is valid as long as the "depth of penetration" of the cooling is small compared with the diameter of the tube. Since, however, by far the greatest error is made because of the variation of the thermometric conductivity, it can be used

as an approximation if depth of penetration and tube diameter are comparable. For greater exactness,  $k$  must be introduced as an entity dependent on the temperature, a fact, however, that excludes a general integration of the heat-conductivity equation in a complete form. For a gas mass that at the time  $t = 0$  has the temperature  $T_1$  and is brought in contact with a plane wall<sup>1</sup> at a constant temperature of  $T_0$ , the following is valid for the temperature distribution at the time  $t$ , if we let the positive  $x$ -axis coincide with the direction of the normal from the wall into the gas,<sup>2</sup>

$$T = T_0 + (T_1 - T_0)\psi\left(\frac{x}{2\sqrt{kt}}\right) \quad (70)$$

where  $k$  has the earlier meaning and  $\psi$ , the Gaussian integral of error, is defined by

$$\psi(\xi) = \int_0^\xi e^{-\eta^2} d\eta$$

For various values of  $kt$ , we obtain a "depth of penetration"  $\Delta x$ , up to which point an appreciable cooling of the gas has taken place of the above order of magnitude. Of course, what should be regarded as an appreciable cooling is somewhat arbitrary. A cooling of about  $50^\circ\text{C}$  can certainly be regarded as considerable, but at  $T_1 - T_0 = 2000^\circ$  it amounts to only 2.5 per cent. The associated value of  $x/2\sqrt{kt}$  would be about 1.6; with  $k = 1 \text{ cm}^2/\text{sec}$ , would result in

$$\Delta x \cong \sqrt{3.2 \cdot 5 \cdot 10^{-4}} = 0.4 \text{ mm}$$

which is much the same value as above if we retain the numerical values for  $k$  and  $t$ . Since the thermometric conductivity at high temperatures, particularly in gases rich in hydrogen, can be many times more than the values assumed above, the depth of cooling is hardly estimated too high.

Another factor affects the flame velocity (and hence indirectly the location of the ignition limits) in narrow tubes and therefore for very convex burning surfaces. The propagation velocity in a convex burning surface with a small radius must be smaller than that in a plane burning surface for the simple reason that, in a greatly curved surface, one element of the burning zone must furnish a greater volume of fresh gas with heat (and free radicals) than in a plane surface (Fig. 91). The deceleration of the combustion velocity with a greatly curved convex



FIG. 91.

<sup>1</sup> It can be demonstrated that the temperature of the wall does not change markedly even on the surface when the flame front passes.

<sup>2</sup> Cf. FRANK-MISES, "Differential- und Integralgleichungen der Physik." Gauss's integral of error can be found tabulated in Jahnke-Emde, "Tables of Functions."

burning surface is, with the opposite sign, the same effect that causes a considerable increase in the combustion velocity with greatly curved concave burning surface, because a smaller volume of fresh gas with heat and free radicals is to be furnished (Fig. 91). As the direct result of this effect, we notice (Fig. 92) that the inner cone of a Bunsen burner does not end in a point but is rounded off, because, in the neighborhood of the point with concave and greatly curved burning surface, the combustion velocity is well above its normal value (*cf.* page 78).

Mathematically this is expressed (*cf.* page 77) by having the heating velocity, which is expressed in the one-dimensional case by

$$\frac{\partial T}{\partial l} = k \frac{\partial^2 T}{\partial r^2} \quad (71)$$

expressed in the three-dimensional, spherically symmetrical case by

$$\frac{\partial T}{\partial l} = k \left( \frac{\partial^2 T}{\partial r^2} + \frac{2}{r} \frac{\partial T}{\partial r} \right) \quad (72)$$

If (Fig. 93) the burning surface is convex,  $2/r \partial T/\partial r$  becomes negative and effects a decrease in the heating velocity of the fresh gas; in a concave burning surface,  $\partial T/\partial r$  becomes positive and aids the heating of the fresh gas. The formal expression for the diffusion of active particles is the same. Numerically we obtain (as a preliminary estimate) the following: if  $T_1 - T_0 \cong 2000^\circ$  and the thickness of the burning zone is about  $10^{-2}$  cm, then as an average

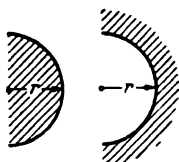


FIG. 93.

and

$$\frac{\partial T}{\partial r} \cong 2 \cdot 10^5 \text{ deg/cm}$$

$$\frac{\partial^2 T}{\partial r^2} \cong 2 \cdot 10^7 \text{ deg/cm}^2$$

The member  $2/r \partial T/\partial r$  together with the first member in (72) is thus negligible if

$$\frac{2}{r} \ll 10^2 \text{ cm}^{-1}$$

in other words, if  $r > 2 \cdot 10^{-2}$  cm. With radii of the order of magnitude of several tenths of a millimeter, the influence of the curvature of the burning surface will be considerable and, at 1 mm or even above, will be just noticeable.

In the immediate proximity of the ignition limit, these influences can have an even greater effect. From all this, it is not surprising that experiments show a dependence of the ignition limits on the size of the



FIG. 92.—Rounding of the point of a Bunsen burner as a result of the heat (and diffusion) current increased there.



container. To be sure, conduction and diffusion are not the only influences that make themselves felt. In general, ignition in a vertical tube propagates more easily from below to above than from above to below because in one case convection favors it and in the other it hinders it. Ignition in a horizontal tube yields, as can be expected, average results. The influence of convection is clearest in the ignition of hydrogen-air mixtures in a vertical tube.<sup>1</sup>

Insofar as no special provision is made, the ignition limit is not independent of the type of ignition used. We have seen in Chap. II, page 58, how the minimum energy required for spark ignition varies with the composition of the gas. For practical application, it is necessary to determine the ignition limits in such a manner as to make it possible in using nonignitable mixtures actually to get outside the danger zone. We shall define the ignition limits under such circumstances as those below which ignition occurs extremely easily, *i.e.*, in a not too narrow (several centimeters wide) vertical tube, with ignition from below and with a sufficiently strong spark. What a sufficiently strong spark might be must be determined by experiment, or we may convince ourselves in determining the ignition limit itself by observing whether, when increasing the spark energy, no further displacement of the ignition limit takes place. On the other hand, care must be taken to note

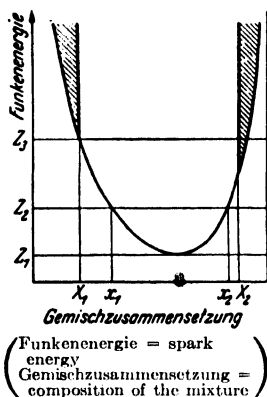


FIG. 94.—Relations between spark energy  $Z$  and ignition limits ( $X_1$  and  $X_2$ , true ignition limits). [From Lindeijer, *Rec. trav. chim.* vol. 56 (1937).]

that actual ignition takes place, *i.e.*, that the combustion is propagating some distance from the point of ignition; for, in the proximity of the source of ignition, it is always possible with sufficient energy to force a more or less intensive conversion. This means, however, that we cannot use too high an ignition energy; in any case, it must be small in proportion to reaction energy present in the total gas mass. Practically, this can be achieved by igniting the gas in a tube that is not too short and by regarding as ignition only those cases in which the flame has propagated itself through the entire tube.

The conditions in determining ignition limits with sparks of varying energy have been discussed in greater detail by Lindeijer<sup>2</sup> (Fig. 94). Here the composition of the mixture (about  $x$  per cent fuel in air) is plotted as the abscissa and the spark energy  $Z$  as the ordinate. Not a single mixture will be ignited if the spark energy is under  $Z$ ; if it is

<sup>1</sup> Cf. CLUSIUS, K., and H. GUTSCHMIDT, *Z. Elektrochem.*, **42**, 498 (1936).

<sup>2</sup> LINDEIJER, E.W., *Rec. trav. chim.*, **56**, 97, 105 (1937).

increased to about  $Z_2$ , with this energy the limits  $x_1$  and  $x_2$  would be obtained. The actual ignition limits lie at  $X_1$  and  $X_2$ . To reach them, the spark energy would have to be increased to  $Z_3$ . If we ignite with this or a higher energy in case we reach the shaded portions, we still obtain a flame in the neighborhood of the spark, but the flame is extinguished at some distance; whereas only within  $X_1$  and  $X_2$  does the flame propagate over any distances. Since one can never know in industries endangered by explosion how great the ignition energy can be, it is necessary in determining the ignition limits to raise the spark energy to over  $Z_3$  in order to obtain the true limits.

In Tables 22 to 26, we present a survey of the ignition limits obtained by experiment. As is to be expected, the ignition limits vary when the initial temperature and pressure are varied. Raising the temperature seems to widen the limits without exception. In ignition at the top of a vertical tube, White<sup>1</sup> found the limits for hydrogen, carbon monoxide, and methane in air given in Table 22.

TABLE 22.—IGNITION LIMITS IN DEPENDENCE ON THE TEMPERATURE (FROM WHITE)

| Temperature                          | 17°C | 100°C | 200°C | 300°C | 400°C |
|--------------------------------------|------|-------|-------|-------|-------|
| Lower limit, % H <sub>2</sub> .....  | 9.4  | 8.8   | 7.9   | 7.1   | 6.3   |
| Upper limit, % H <sub>2</sub> .....  | 71.5 | 73.5  | 76    | 79    | 81.5  |
| Lower limit, % CO.....               | 16.3 | 14.8  | 13.5  | —     | 11.4  |
| Upper limit, % CO.....               | 70   | 71.5  | 73    | —     | 77.5  |
| Lower limit, % CH <sub>4</sub> ..... | 6.3  | 5.95  | 5.50  | —     | 4.80  |
| Upper limit, % CH <sub>4</sub> ..... | 12.9 | 13.7  | 14.6  | —     | 16.6  |

The relation between ignition limits and pressure does not seem to be definite. As we have already seen, increase in pressure does not in general increase the linear combustion velocity, but it does increase the "mass-burning velocity," i.e., the mass converted in a unit of time. Since the reaction velocity almost always rises with the pressure at not too low a pressure (upper explosion limit; cf. Chap. VIII), we should consider it extremely probable that the ignition limits also would widen with an increase in pressure at not too low a pressure, whereas for low and medium pressures no definite general predictions can be made. These conjectures, at least for very high temperatures, seem to be corroborated by experiment.<sup>2</sup>

<sup>1</sup> Cf. BONE, W.A., and D.T.A. TOWNEND, "Flame and Combustion in Gases," London, 1927.

<sup>2</sup> On the influence of the pressure on the ignition limits, cf. also D.M. Newitt, and D.T.A. Townend, "The Science of Petroleum," Vol. IV, pp. 2884ff.

Terres and Plentz<sup>1</sup> found the following limits for hydrogen, methane, and carbon monoxide mixed with air:

|                                       |           |                |           |
|---------------------------------------|-----------|----------------|-----------|
| H <sub>2</sub> -air at 1 atm, %.....  | 9.0-68.5  | At 10 atm..... | 9.5-67.5  |
| CH <sub>4</sub> -air at 1 atm, %..... | 6.0-13    | At 10 atm..... | 6.6-14    |
| CO-air at 1 atm, %.....               | 15.9-72.9 | At 10 atm..... | 18.4-62.4 |

Here a widening of the upper limits takes place only in methane; in other cases, an increase in pressure effects a narrowing of the limits, which is the most pronounced in carbon monoxide. This refers, however, to relatively low pressures. If higher pressures are considered, the limits are considerably widened, at least in the case of methane-air, as can be seen in the following compilation by Berl and Werner (Table 23).<sup>2</sup>

TABLE 23.—IGNITION LIMITS FOR METHANE IN AIR AT VARIOUS PRESSURES (FROM BERL AND WERNER)

| p, atm | % Methane   |             |
|--------|-------------|-------------|
|        | Lower limit | Upper limit |
| 1      | 6.6         | 12.7        |
| 21     | 7.5         | 12.0        |
| 400    | 5.2         | 46.0        |

In this case also, there is a narrowing of the ignition range at moderately high temperatures but a considerable widening at very high pressures. The values for methane were in the main corroborated by Bone and associates (cited page 156) in a pressure range up to 125 atm. They also found a widening of the ignition range with increased pressure for hydrogen-air mixtures, although only at the upper limit. The lower limit remained constant (*cf.* Table 24).

On the other hand (according to the same authors), the ignition limits narrow with increased pressure in the case of carbon monoxide-air mixtures even at 125 atm (*cf.* Table 25).

If, in carbon monoxide-air mixtures, helium or argon replaces the nitrogen, the ignition limits are extended, just as vapor causes an appreciable widening of the ignition limits (Bone, cited page 156). Here it is again demonstrated that factors which increase the combustion velocity at the same time widen the ignition limits.

A very valuable survey of the ignition temperatures and their practical

<sup>1</sup> TERRES and PLENTZ, *Gas- u. Wasserfach*, **57**, 995, 1016, 1024 (1914). *Cf.* also MASON and WHEELER, *Trans. Chem. Soc.*, **113**, 45 (1918). BONE, NEWITT, and TOWNEND, "Gaseous Combustion at High Pressures," London, 1929.

<sup>2</sup> BERL, G., and G. WERNER, *Z. angew. Chem.*, **40**, 245 (1927).

application in industries endangered by explosion is given by Jones.<sup>1</sup> We wish to call special attention to his work and take from it the observation by Burgess and Wheeler<sup>2</sup> that in many cases a simple relation exists between the heating value of a fuel and the lower limit of ignition. The lower ignition limit multiplied by the heat of combustion of the fuel approaches a constant (whose value for hydrocarbons lies in the neighbor-

TABLE 24

| $p$ ,<br>atm | % H <sub>2</sub> in air at the<br>upper ignition<br>limit |
|--------------|---|
| 5            | 68.4  |
| 10           | 68.5  |
| 30           | 71.9  |
| 50           | 73.3  |
| 75           | 74.2  |
| 125          | 74.8  |

TABLE 25

| $p$ ,<br>atm | % CO in air          |                      |
|--------------|----------------------|----------------------|
|              | Lower ignition limit | Upper ignition limit |
| 1            | 14.2                 | 71                   |
| 5            | 15.4                 | 67.5                 |
| 10           | 17.8                 | 62.8                 |
| 30           | 20.3                 | 58.8                 |
| 50           | 20.6                 | 56.8                 |
| 125          | 20.7                 | 51.6                 |

hood of 1100, if the ignition limit is expressed by the percentage of fuel in air and the heat of combustion is expressed in kcal/mol). This relation can at least be useful for an estimate of the lower ignition limit of substances not yet investigated in detail, just as Le Chatelier's rule<sup>3</sup> is useful in estimating the limits for mixtures. This is simply the application of the mixing rule to fuel mixtures and is generally given in the form

$$L = \frac{100}{P_1/N_1 + P_2/N_2 + \cdots}$$

where  $L$  is the ignition limit for the fuel mixture from the components 1, 2, . . . ,  $N_1$ ,  $N_2$ , . . . are the corresponding ignition limits of these pure components (in per cent) and  $P_1 + P_2 + \cdots = 100$ . A validity even only approximately exact can of course not be expected in the case of fuels that exert a strong influence on each other in combustion. When small or even great variations are noted, therefore, it is not necessary to look for a special explanation. An explanation would be necessary only if one found a general validity of Le Chatelier's rule contrary to expectations. The rule will apply most accurately when the materials to be investigated are most similar. These happen to be the most interesting cases from a practical point of view, *e.g.*, hydrocarbon mixtures, mixtures of organic solvents. Here Le Chatelier's rule can often be useful for a preliminary estimate.

<sup>1</sup> JONES, G.W., *Chem. Rev.*, **22**, 1 (1938).

<sup>2</sup> BURGESS, M.J., and R.V. WHEELER, *J. Chem. Soc.*, **99**, 2013 (1911).

<sup>3</sup> LE CHATELIER, H., and O. BOUDOUARD, *Compt. rend.*, **126**, 1344, 1510 (1898).

TABLE 26.—IGNITION LIMITS IN AIR (FROM JONES)

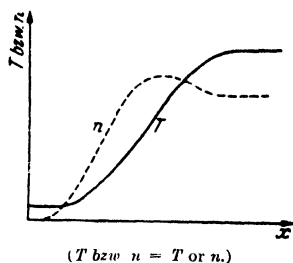
| Material                | Ignition limit,<br>vol. % |       | Material  | Ignition limit,<br>vol. % |       |
|-------------------------|---------------------------|-------|---|---------------------------|-------|
|                         | Lower                     | Upper |   | Lower                     | Upper |
| Methane.....            | 5.00                      | 15.00 | Acetone.....  | 2.55                      | 12.80 |
| Ethane.....             | 3.22                      | 12.45 | Methyl ethyl ketone....                               | 1.81                      | 9.50  |
| Propane.....            | 2.37                      | 9.50  | Methyl propyl ketone....                              | 1.55                      | 8.15  |
| Butane.....             | 1.86                      | 8.41  | Methyl butyl ketone....                               | 1.22                      | 8.00  |
| Isobutane.....          | 1.80                      | 8.44  |   |                           |       |
| Pentane.....            | 1.40                      | 7.80  | Methyl formate.....                                   | 5.05                      | 22.70 |
| Isopentane.....         | 1.32                      | —     | Ethyl formate.....                                    | 2.75                      | 16.40 |
| Hexane.....             | 1.25                      | 6.90  | Methyl acetate.....                                   | 3.15                      | 15.60 |
| Heptane.....            | 1.00                      | 6.00  | Ethyl acetate.....                                    | 2.18                      | 11.40 |
| Octane.....             | 0.95                      | —     |   |                           |       |
| Nonane.....             | 0.83                      | —     | Propyl acetate.....                                   | 2.05                      | —     |
| Decane.....             | 0.67                      | —     | Isopropyl acetate.....                                | 2.00                      | —     |
|                         |                           |       | Butyl acetate.....                                    | 1.70                      | —     |
| Ethylene.....           | 2.75                      | 28.60 | Amyl acetate.....                                     | 1.10                      | —     |
| Propylene.....          | 2.00                      | 11.10 |   |                           |       |
| Butylene.....           | 1.70                      | 9.00  | Hydrogen.....   | 4.00                      | 74.20 |
| Amylene.....            | 1.60                      | —     | Carbon monoxide.....                                  | 12.50                     | 74.20 |
|                         |                           |       | Ammonia.....  | 15.50                     | 27.00 |
| Acetylene.....          | 2.50                      | 80.00 |   |                           |       |
|                         |                           |       | Ethylene oxide.....                                   | 3.00                      | 80.00 |
| Benzol.....             | 1.41                      | 6.75  | Propylene oxide.....                                  | 2.00                      | 22.00 |
| Toluyl.....             | 1.27                      | 6.75  | Dioxane.....  | 1.97                      | 22.25 |
| <i>o</i> -Xylol.....    | 1.00                      | 6.00  | Diethyl peroxide.....                                 | 2.34                      | —     |
|                         |                           |       |   |                           |       |
| Cyclopropane.....       | 2.40                      | 10.40 | Carbon disulphide.....                                | 1.25                      | 50.00 |
| Cyclohexane.....        | 1.33                      | 8.35  | Hydrogen sulphide.....                                | 4.30                      | 45.50 |
| Methyl cyclohexane....  | 1.15                      | —     | Carbon oxysulphide....                                | 11.90                     | 28.50 |
|                         |                           |       |   |                           |       |
| Methyl alcohol.....     | 6.72                      | 36.50 | Methyl chloride.....                                  | 8.25                      | 18.70 |
| Ethyl alcohol.....      | 3.28                      | 18.95 | Vinyl chloride.....                                   | 4.00                      | 21.70 |
|                         |                           |       | Ethyl chloride.....                                   | 4.00                      | 14.80 |
| Propyl alcohol.....     | 2.55                      | —     | Amyl chloride.....                                    | 1.40                      | —     |
| Isopropyl alcohol.....  | 2.65                      | —     |   |                           |       |
| Butyl alcohol.....      | 1.70                      | —     | Acetylene dichloride                                  |                           |       |
| Isobutyl alcohol.....   | 1.68                      | —     | (C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub> )..... | 9.70                      | 12.80 |
| Amyl alcohol.....       | 1.19                      | —     | Ethylene dichloride                                   |                           |       |
| Isoamyl alcohol.....    | 1.20                      | —     | (C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> )..... | 6.20                      | 15.90 |
|                         |                           |       | Methyl bromide.....                                   | 13.50                     | 14.50 |
| Acetaldehyde.....       | 3.97                      | 57.00 | Ethyl bromide.....                                    | 6.75                      | 11.25 |
|                         |                           |       |   |                           |       |
| Methyl ethyl ether..... | 2.00                      | 10.10 |   |                           |       |
| Diethyl ether.....      | 1.85                      | 36.50 |   |                           |       |
| Divinyl ether.....      | 1.70                      | 27.00 |   |                           |       |

For many practical conclusions, we refer to the original work by Jones in Table 26. For literature as well as for other information, see the work by Jones as well as by Landolt-Börnstein, the "Tables Annuelles" and Bone and Townend, "Flame and Combustion in Gases."

**9. Influence of Mixtures on Ignition Limits.**—There is extensive experimental material covering the influence of mixtures on ignition limits. We have already mentioned certain observations elsewhere (*cf.* the ignition limits of fuel-air, and fuel-oxygen, page 110). Some observations can also be gained from the investigations of combustion velocities by Bunte and associates (*cf.* the notes on pages 72, 121), *e.g.*, the narrowing of the ignition limits when  $\text{CO}_2$  is substituted for air-nitrogen and, conversely, the limits are widened by substituting rare gases for nitrogen (*cf.* page 130).

The question regarding the influencing of the ignition limits is in many respects of importance, especially, of course, with reference to the prevention of explosion. Working with combustible gases and damps cannot be avoided, but any danger of explosion would be excluded from the start if it were possible to put them beyond the range of ignition when mixed with air by mixing them with suitable substances. Because of the fundamental nature of this question, we shall consider whether a theoretical prediction in this

direction can be made. We know (Chaps. VIII, IX, and XI) that the explosion limits for the spontaneous ignition of gas mixtures can be changed considerably by the addition of small quantities of chain-breaking substances. The most practical example of the suppression of spontaneous reactions is the effect of the antiknock compounds, especially that of lead tetraethyl. In the effect of these substances, the following seems to take place (something like Fig. 87): If we imagine the reaction velocity for a reaction of that kind plotted as a function of time, we shall obtain the usual course. The rise in velocity, at least for the initial stage, is in many cases conditioned by the rise in concentration of active particles,  $n$ , which is due to chain-branching (*cf.* Chap. VIII). In the very beginning, there are only very few of these active particles, and if they can be eliminated by means of suitable substances, chain-branching is averted and the explosion is obviously suppressed. That this can be achieved under certain circumstances with very small quantities of added material is perhaps due to the fact that these materials are effective at a very early stage of conversion when the concentration of active particles is still small. Lead tetraethyl is effective in concentrations of about  $10^{-5}$  in relation



( $T$  bzw  $n = T$  or  $n$ .)  
FIG. 95.—Variations in the temperature and concentration  $n$  of active particles in the flame front, schematic.

to the fuel. If we now attempt to prevent the propagation of an explosion by means of the same materials, the result is shown in Fig. 95. We again draw the structure of the flame front in the usual way. Near  $T$  the concentration of active particles,  $n$ , is shown. Obviously the material that has been added in small amount could, in the zone of lower temperature and lower concentration of active particles, snatch these

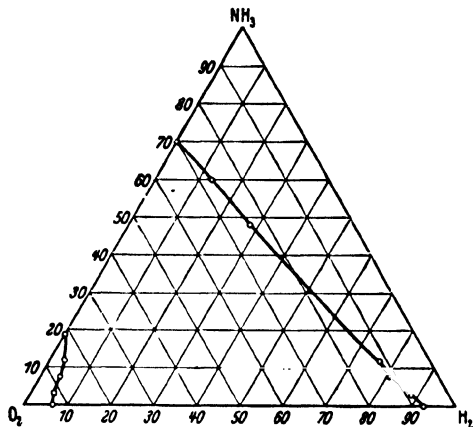


FIG. 96.—Ignition range of the system  $\text{H}_2\text{—O}_2\text{—NH}_3$ . (From Jorissen and Onkiahong, *Rec. trav. chim.*, vol. 45.)

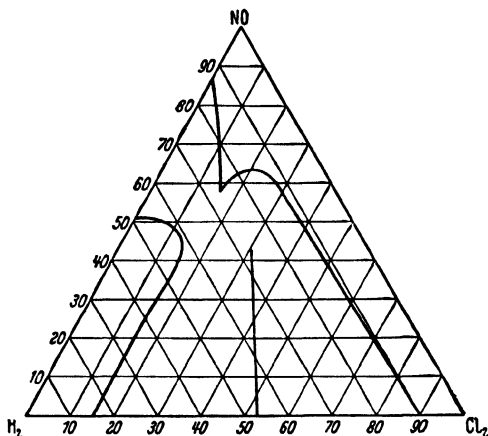


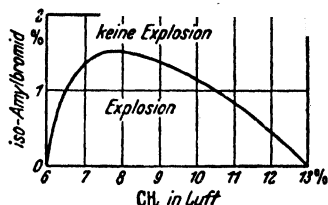
FIG. 97.—Ignition range of  $\text{H}_2\text{—NO—Cl}_2$ . [From Jorissen, *Chem. Weekblad.*, vol. 33 (1936).]

particles away and suppress the reaction. The difference from spontaneous ignition consists in this, however, that in the latter the reaction is actually suppressed with the snatching away of the first centers of activity; whereas, in the hotter neighboring layers, new centers constantly are added by diffusion, the concentration of which, especially in the hot burned gases will never fall below the equilibrium value. As

a result, it is to be expected that the same small additions can, to be sure, occasionally reduce the flame velocity somewhat (*cf.* page 122) but in such small concentrations that they will be able to influence the ignition limits very little.

Ignition limits of mixtures have been investigated especially by Jorissen and associates.<sup>1</sup> Several examples are offered. Figure 96 shows the system  $\text{NH}_3\text{—H}_2\text{—O}_2$ .<sup>\*</sup> Figure 97 shows the system  $\text{H}_2\text{—NO—Cl}_2$  with a remarkable pattern of the limits.

Of special interest, naturally, are the experiments on the effect of small additions (Jorissen, Booy, and van Heiningen, cited page 135; Jorissen and Hermans, cited page 135). For the suppression of methane explosions, ethyl iodide and silicon tetrachloride were relatively effective;  $\text{POCl}_3$  was most effective. In Fig. 98, we present the explosion range for methane-air-iso-amylbromide, from which the relative effectiveness of this substance can be seen.



(keine Explosion = no explosion)  
in Luft = in air

FIG. 98.—Ignition range of  $\text{CH}_4\text{—air—iso-amylbromide}$ . [From Jorissen and Hermans, *Rec. trav. chim.*, vol. 52 (1933).]

Other organic halides have a similar effect. In the data of Fig. 98, it should be observed that we are dealing with percentages of amylbromide in a fuel-air mixture, not related to the fuel alone; in spite of that fact, the effective additions are relatively low.

Ignition limits for the mixture ethylene-oxide-air with a mixture of  $\text{CO}_2$  are given by Peters and Ganter.<sup>2</sup> The ignition ranges for a number of fuel systems are also compiled in the monograph by Lewis and v. Elbe (cited page 137). For the influence of hydrogen on explosion, *cf.* Nagai,<sup>3</sup> and for the fundamental question of extinguishing, *cf.* Dufraisse.<sup>4,5</sup>

<sup>1</sup> JORISSEN, W.P., Numerous works in *Rec. trav. chim.* since 1924; of more recent works, see, among others, K. Posthumus, *Rec. trav. chim.*, **49**, 309 (1930). BOOY, J., *Rec. trav. chim.*, **49**, 866 (1930). JORISSEN, BOOY, and J. VAN HEININGEN, *Rec. trav. chim.*, **49**, 877 (1930). JORISSEN and BELINFANTE, A.H., *Rec. trav. chim.*, **51**, 853 (1932). JORISSEN, BOOY, and VAN HEININGEN, *Rec. trav. chim.*, **51**, 868 (1932). JORISSEN and J.J. HERMANS, *Rec. trav. chim.*, **52**, 271 (1933). JORISSEN and A.A. VAN DER DUSSEN, *Rec. trav. chim.*, **52**, 327 (1933). JORISSEN, A.A. VAN DER DUSSEN, W.P.M. MATLA, and J.H. DE LIEFDE, *Rec. trav. chim.*, **52**, 403 (1933). J.J. VAN DER WAL, *Rec. trav. chim.*, **53**, 97 (1934). DROP, J., *Rec. trav. chim.*, **54**, 671 (1935). JORISSEN, *Rec. trav. chim.*, **54**, 888 (1935). DROP, J., *Rec. trav. chim.*, **56**, 71, 86 (1937). LINDEIJER, E.W., *Rec. trav. chim.*, **56**, 97, 105 (1937). JORISSEN, *Chem. Weekblad.*, **33**, 83 (1936).

<sup>\*</sup> JORISSEN, W.P., and B.L. ONKIEHONG, *Rec. trav. chim.*, **45**, 228 (1926).

<sup>2</sup> PETERS, G., and W. GANTER, *Z. angew. Chem.*, **51**, 29 (1938).

<sup>3</sup> NAGAI, *Rept. Aeronaut. Research Inst. Tôkyo Imp. Univ.*, **2**, 249, 259, 275 (1927); *Proc. Imp. Acad. Tôkyo*, **4**, 154 (1928).

<sup>4</sup> DUFRAISSE, C., and J. LEBRAZ, *Compt. rend.*, **199**, 75 (1934).

<sup>5</sup> Ternäre and quaternäre Zundgebiete, see also A. la Fleur, *Rec. trav. chim.*, **56**, 433 (1937).



## CHAPTER IV

### EXPLOSIONS IN CLOSED CHAMBERS

#### 1. Summary of Flame Propagation Phenomena in Closed Chambers.

It has been convenient for the time being to omit all complications that are affected by a change of pressure during combustion. Thus flame propagation in closed chambers was excluded from consideration in the preceding chapter. In addition to the change in pressure, which brings into play not merely one value for the combustion velocity but rather a multiplicity of combustion velocities at various pressures and temperatures, the gas currents in such cases are also generally more complicated than in open tubes. These phenomena, which are naturally very important for their practical application, will now be considered.

The expansion of the burning gases results in a characteristic movement of each element of the gas. Let us imagine (Fig. 99) the explosive

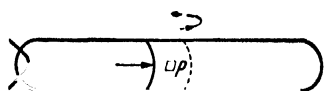


FIG. 99.

mixture enclosed in a tube and ignited at the left end. A gas particle in the tube, let us say at  $P$ , is, as long as the flame has not yet reached it, driven to the right by the expanding gases. From the moment in which the flame front has passed the volume element at  $P$ , it will move to the left, *i.e.*, always away from the burning zone; for now the gas expands to the right, while that to the left is compressed. As long as no uneven cooling takes place and no oscillations occur, it would have to come to rest again finally at  $P$ .<sup>\*</sup> The same is true for the spread of the flame in a sphere, with ignition at the center. Here the cooling, up to the end of the combustion, is relatively much less than in a tube, since the hot combustion gases touch the wall only after complete combustion, and since the heat conduction from the inside does not travel more rapidly than the flame. As long as the flame has not yet reached the wall, no direct loss of heat by conduction takes place; loss of heat occurs solely by radiation, and conduction comes into play only indirectly. The unburned fresh gas is adiabatically compressed by the expanding burning gases and thus heated. A part of this heat can be given off to the outside by conduction. The compression of the fresh gas by the expanding burning gas and the compression of the gas burned at first by the gas

<sup>\*</sup> We shall see later that, even when cooling is disregarded, a fundamentally uneven temperature distribution results; therefore the gas particle cannot come to rest exactly in its former position.

burning later also cause a temperature decrease within the burned gases to such an extent that the gas burned at first (the inside of the spherical bomb) is hotter at completed combustion than the part burned last—indeed, under certain circumstances, considerably hotter, sometimes by hundreds of degrees (up to  $900^{\circ}$ ).<sup>1</sup> Because of this temperature gradient, the maximum pressure in an explosion in a closed bomb is continuously a little lower than the value theoretically possible at an evenly distributed temperature. The reason for this is the increase in specific heat with the temperature. The fact that the temperature at the end of the combustion is considerably higher in the neighborhood of the place of ignition than at a distance from it has the further effect of causing the hot gases to flame up greatly there once more toward the end of the combustion. This phenomenon is often observed and is known as “after-burning,”<sup>2</sup> because it was at first assumed that another reaction took place. Apparently, however, the existence of the great temperature gradient suffices to explain completely all observed phenomena (Lewis and v. Elbe), even the fact that “after-burning” gases are able to ignite new fresh gas; for the hot after-burning gases will carry along, in addition to their heat energy, free radicals present in the thermal equilibrium.

How the temperature gradient arises can be thought of qualitatively in the following manner, according to Lewis and v. Elbe. The combustion of every thin layer of gas (cf. page 148) can be regarded as taking place at practically constant pressure, namely, the prevailing pressure at which the layer of gas expands from an initial volume to a terminal volume, which stands in the relation of the initial temperature  $T_a$  to the end temperature  $T_b$  reached in the moment of combustion<sup>3</sup> in general, because of the compression effects already discussed ( $T_a$  and  $T_b$  are not identical with the initial temperature of the entire gas  $T_0$  and its average terminal temperature  $T_c$ ). Specifically, a volume of gas at the point of ignition will burn under the initial pressure  $p_0$ , and a volume in immediate proximity to the wall will burn under the terminal pressure  $p_e$ . The volume in the center performs work on the surrounding gas mass during the expansion at the pressure  $p_0$ . In other words, it is then again compressed to approximately its initial volume by a pressure rise from

<sup>1</sup> First demonstrated experimentally by Hopkinson [*Proc. Roy. Soc. London, A*, **77**, 387 (1906)], theoretically treated by Flamm and Mache [*Wien. Ber.*, **126**, 9 (1917)]. Cf. also MACHE, H., “Die Physik der Verbrennungserscheinungen.” LEWIS, B., and G. v. ELBE, *J. Chem. Phys.*, **2**, 659, 665 (1934). Also “Combustion, Flames and Explosions of Gases.” Such a decrease in temperature appears also in the combustion of engines (cf. Chap. XII).

<sup>2</sup> ELLIS, O.C. DE C., and R.V. WHEELER, *J. Chem. Soc.*, 1927, p. 310; 1931, p. 2467. ELLIS, O.C. DE C., and E. MORGAN, *Trans. Faraday Soc.*, **30**, 287 (1934).

<sup>3</sup> Multiplied by a factor that takes account of the change of the mol-number in case the reaction takes place during a change of the mol-number.

$p_0$  to  $p_c$ , the average being at essentially higher pressures. As a result, the volume element gives off less energy to the remaining gas mass than it later takes up again. It must therefore be hotter at the end than the average temperature of the entire gas mass. Conversely, a volume element near the edge is compressed at pressures between  $p_0$  and  $p_c$ , but it expands again at the highest pressure  $p_c$ . As a result, it gives off more energy at expansion than it has taken up during compression. It will therefore be colder at the conclusion than its average temperature.

According to Lewis and v. Elbe, this temperature gradient expresses itself in a characteristic manner in the cooling curve obtained in bomb explosions, namely (Fig. 100), by a hump at A. At the moment in which the burning zone has reached the wall, there is first of all a considerable cooling, at 1 in Fig. 100. The cooling velocity would then

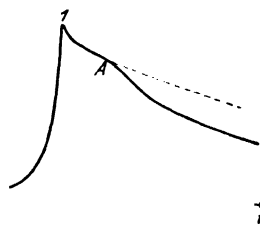


FIG. 100.—Pressure-time curve in bomb explosions, schematic. (From Lewis and v. Elbe.)

decrease, and there would be an exponential decrease of the temperature (dotted curve). Actually, however, the stronger heat flow that comes from the inner hotter layers now becomes noticeable. Once more there is a strong decrease in temperature and only then an approximately exponential decline. In the actual pressure diagrams of bomb explosions, this course of events is clearly visible only when the conductivity is relatively large and the time of cooling short. When the conductivity is low, the curve is extended in

the direction of the time axis; and the hump at A, although present, is not very striking.

In addition to the effects of compression, which can generally be neglected in open chambers (except in the case of flames with a velocity greater than sound or in the case of detonations), the currents of the gas as a whole as well as the shock waves resulting from the progress of the flame in combustion in closed chambers play an even more important role (*cf.* on this point Chap. V). Because of these phenomena, photographs are obtained like those in Figs. 101*a* and 101*b* with not too slowly burning gas mixtures ignited in closed chambers. In one photograph, the combustion of  $2\text{CO} + \text{O}_2$  is shown in a horizontal tube 35 cm in length and 2 cm in diameter with ignition at one end. In the other, the flame was photographed in a mixture consisting of 12 parts of acetylene and 88 parts of a mixture of  $2\text{CO} + \text{O}_2$  with ignition in the middle of the tube. Both photographs show the same thing. The progressing flame, initially accelerated, is suddenly and so greatly retarded that the direction of propagation is momentarily reversed. This phenomenon repeats several times. The reason for this can easily be seen by observing

the photograph of the burned gases, a zigzag track along which the burned gases flame up again and again. From the gradient of the path, values for the velocity of this process of the order of magnitude of 1000 m/sec result, *i.e.*, the order of magnitude of the velocity of sound in the burned gases. The velocity gradually declines, chiefly as the result of the cooling of the gases, as can be seen from the ever-increasing inclination of the zigzag track. Only one shock wave comes into consideration as a



FIG. 101a.—Flame of  $2\text{CO} + \text{O}_2$  at ignition at the end of a closed tube; vertical lines at intervals of 5 cm, vertical time marks in  $\frac{1}{1000}$  sec. (From Bone and Fraser.)

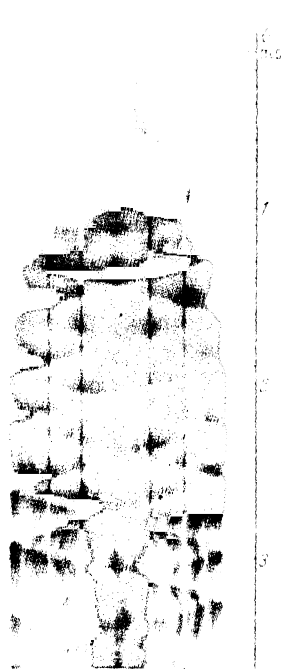


FIG. 101b.—Flame of  $12\text{C}_2\text{H}_2 + 88(2\text{CO} + \text{O}_2)$  at ignition in the center of a closed tube. [From Bone and Fraser, *Phil. Trans. Roy. Soc. London*, vol. 228 (1928).]

process that propagates with this velocity. Its velocity is dependent on the shock pressure and is always greater than the velocity of sound (*cf.* Chap. V). If the shock pressure is small, the velocity of the shock wave is only a little greater than that of sound, which can generally be assumed for shock waves accompanying flames in closed tubes.

It was formerly assumed that these shock waves had their origin in the ignition spark. Normally, however, this might not be the case. To be sure, every spark may initiate a shock wave; but the amplitude of the latter is in general too small to be responsible for the observed disturbances. Rather, the accelerated progressing flame is itself the

cause of the more intensive shock wave. As will be shown in Chap. V, page 164, the compression of a gas in a cylindrical chamber effects the appearing of a shock wave by means of a piston rapidly introduced. This "piston" is in this case the expanding hot combustion gases. Also the appearing of the shock wave can be directly shown experimentally, namely, by means of "schlieren photographs," which, even in non-self-

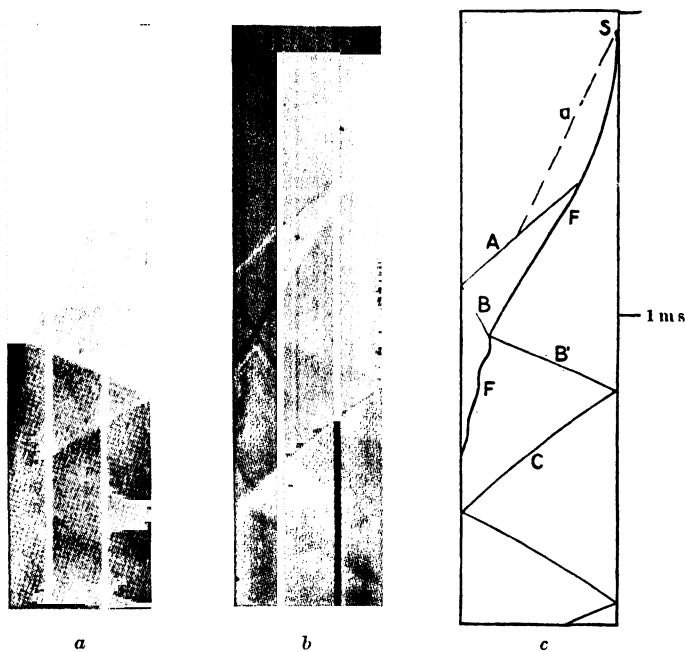
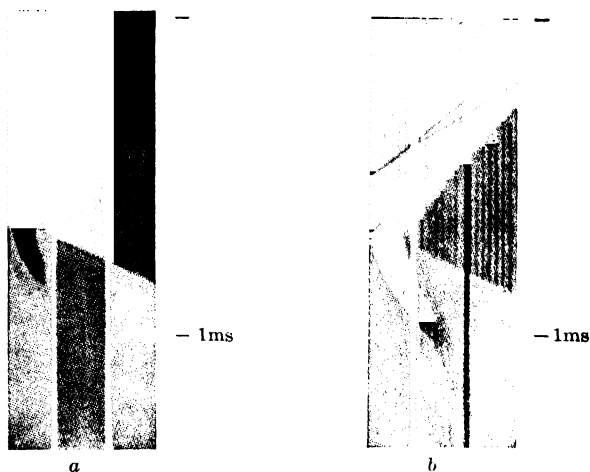


FIG. 102a-c.—Flame photograph ( $15\text{C}_2\text{H}_4 + 85\text{O}_2$ ); at the left, ordinary flame photograph. In the center, schlieren photograph. At the right, sketch of the processes: S, ignition spark; F, flame front; A, percussion wave originating in front of the flame front (after reflection B, B', C, . . .); length of tube 30 cm. (From Payman and Titman, *Proc. Roy. Soc. London*, A, vol. 152.)

illuminating gases, show irregularities of density (Fig. 102).<sup>1</sup> Here photographs of explosions of a mixture of 15 per cent ethylene in oxygen are reproduced. The first photograph is an ordinary flame photograph that shows the well-known disturbances by shock waves. Figure 102b shows the same process, though photographed not by its own light but rather as a "schlieren photograph." Here the same phenomena can be seen as in the preceding photograph; but, in addition, the shock wave that has formed in the unburned gas ahead of the flame front has been reflected

<sup>1</sup> PAYMAN, W., *Proc. Roy. Soc. London*, A, **120**, 90 (1928). PAYMAN, ROBINSON, and SHEPHERD, *Safety in Mines Research Board Papers* 18, 1926; 29, 1927. PAYMAN, W., and H. TITMAN, *Proc. Roy. Soc. London*, A, **152**, 418 (1935). PAYMAN and W. C. FURNESS, *Proc. Roy. Soc. London*, A, **158**, 348 (1937). Cf. also JOUGUET, E., *Chaleur et ind.*, 1939.

at the other end of the tube and has thereafter struck the flame front and disturbed it. As can be seen from Fig. 102, the course of the shock waves is rather complicated. This is due to the fact that, as long as the combustion is not completed, there are gases of different temperatures in which the velocity of sound is also different; in passing through the burning surface, the track of the shock wave is therefore broken. Further, gas currents are present; the compression to which the shock wave owes its origin causes a flow in the fresh gas (which can be proved directly, *cf.* pages 143–144). As a result, the shock wave, by reflection at the



FIGS. 103a and b.—Auto-ignition by a percussion wave in  $2\text{CO} + \text{O}_2$ , which originated spontaneously and was reflected at the left end of the tube. Flame photograph at the left; schlieren photograph at the right. (Length of tube 30 cm.) (From Payman and Titman, p. 139.)

end of the tube, for example, changes its absolute velocity relative to the chamber, since the velocity of the gas flow must be added to the wave velocity relative to the gas at one time but must be subtracted from it at another time. Just as shock waves of greater intensity can lead to the ignition of unburned gases and to detonation (Chap. V, pages 195*ff.*), so the shock waves appearing in the propagation of flames can also sometimes cause an auto-ignition of the gas even without detonation, especially in the reflection of the shock waves at the end of the tube (*cf.* Fig. 103). Observations of this kind are of importance in engine knocking. Such shock waves, by the way, were observed in burning gases very early. The first photographs, which showed all the details, even the oscillating movements of the glowing gas particles, were made by v. Oettingen and Gernet,<sup>1</sup> who photographed the oxygen-hydrogen explosions by means of a rotating mirror in a fixed plate. Since at that time the plates were

<sup>1</sup> V. OETTINGEN, and GERNET, *Ann. Phys. Chem.*, **33**, 586 (1888).

not sensitive enough for this rapid process, they produced a brightly colored, illuminated flame by the addition of copper chloride.

Similar disturbances, but of a much milder sort, might be responsible for the retardation that the movement of a flame experiences after ignition. A flow reflected at the other end of the tube retards the movement of the flame. This backward flow can under certain circumstances be increased by the cooling of the hot gases behind the flame front. A characteristic photograph that shows this phenomenon is reproduced in Fig. 104, after Bone and Fraser (a great number of similar photographs, taken under the most varied conditions, may be found in Bone, cited page 155). The flow responsible for this is shown particularly clearly in photographs by H. Schulze (cf. page 143).

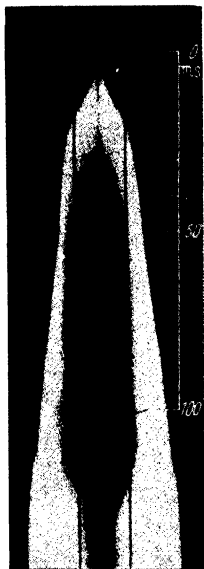


FIG. 104.—Flame photograph of  $\text{CO-O}_2$  with ignition in the center of a closed tube; characteristic retardation of the flame movement; "insert" in the flame picture. [From Bone and Fraser, *Phil. Trans. Roy. Soc. London*, A, vol. 228 (1928).]

If the gas pressure in flames containing shock waves were recorded, an oscillation would be obtained overlapping the normal curve for pressure rise, as it is observed, for example, in knocking combustion in engines. In itself, it is possible that oscillations of that kind appear also in explosions in spherical chambers with ignition in the center. However, gas oscillations as they appear in that kind of explosion are to be differentiated from those caused by shock waves. Such gas oscillations cannot be occasioned by a shock wave caused by a fast flame. Lewis and v. Elbe discuss this phenomenon, which has also been observed by others.<sup>1</sup> Oscillations of that kind appear especially in oxygen-hydrogen explosions with excess nitrogen or oxygen, but not with excess hydrogen or argon. Since it is the slow-burning, not the quick-burning, mixtures that show the oscillations, it is actually quite

improbable that a shock wave initiated by the flame movement could be the cause. Lewis and v. Elbe therefore suggest the following explanation. From measurements on the dispersion of sound, it is known<sup>2</sup> that the stimulus of degrees of freedom of molecules of two or more atoms of oscillation requires time. Until an equilibrium between the kinetic energy of the

<sup>1</sup> LEWIS, B., and G. v. ELBE, *J. Chem. Phys.*, **3**, 63 (1935). Cf. also CAMPBELL, LITTLER, and WHITWORTH, *J. Chem. Soc.*, 1932, p. 339. MORGAN, *Phil. Mag.*, (6), **53**, 1161 (1927). MAXWELL and R. V. WHEELER, *Ind. Eng. Chem.*, **20**, 1041 (1928).

<sup>2</sup> KNESER, *Ann. Physik*, **11**, 761, 777 (1931); **16**, 377 (1933). *Physik. Z.*, **32**, 179 (1931). *Z. Physik*, **77**, 649 (1932). EUCKEN, A., MÜCKE, and R. BECKER, *Naturwissenschaften*, **20**, 85 (1932). EUCKEN, A., and R. BECKER, *Z. physik. Chem.*, Sec. B, **27**, 219, 235 (1934) and others.

movement of the center of gravity and the energy of the oscillations has been effected, up to  $10^6$  gas-kinetic shocks can have occurred in extreme cases. If, for example, at the end of a bomb explosion, the molecular oscillations have not yet been completely stimulated, the energy of the movement of the center of gravity has left a greater share than in equilibrium; and as a result "temperature" and pressure must be somewhat higher at the end than the equilibrium that has come about.<sup>1</sup> If, in the portion of the gas mixture burned first, the oscillation energy is not fully stimulated at the beginning, its temperature and its volume are at first higher than the equilibrium (cf. page 240). When the molecular oscillations are fully stimulated, a contraction is added to the compression that this portion experiences anyhow during the progress of the explosion. It would not be impossible for such a contraction to give rise to the appearance of gas oscillations. This explanation is not absolutely binding—one could also imagine that the stimulus of the inner degrees of freedom and the contraction connected with it would take place so continuously that no oscillations could be stimulated by it—but no other simple explanation can be found for this phenomenon.

Perhaps the following attempt at an explanation is worth considering.<sup>2</sup> If, in a closed container in which a flame is progressing, a weak gas oscillation is stimulated, the reaction velocity is always increased if a densification passes the reaction zone, and thus the rise in pressure is increased. The reverse is true for the troughs of the wave. Waves in such a system must amplify themselves, and it would not be implausible that just such a process took place in slow-burning systems, where the wave often passes across the flame front.

Oscillations of the manometer that was used cannot have simulated this effect. This is a possibility of disturbance that appeared especially in older investigations but can be eliminated by the use of manometers of sufficiently high frequency. In the observations of Lewis and v. Elbe, the same oscillations resulted when various manometers were applied, a direct proof that the oscillations cannot have been due to a property of the manometer.

Since the greater disturbances that are effective as shock waves can be made visible by means of schlieren photographs, direct observations are also possible for the gas currents in milder explosions. Flame photographs that Ellis<sup>3</sup> and associates made according to the method of instantaneous shots show that in closed chambers the flame front assumes remarkable forms that are apparently caused by the compressed fresh gas flowing toward it

<sup>1</sup> WOHL, K., and M. MAGAT, *Z. physik. Chem.*, Sec. B, **19**, 117 (1932).

<sup>2</sup> For the following material, in a somewhat different connection, the author is indebted to H. Schulze, Benzol-Verband, Bochum.

<sup>3</sup> ELLIS, O. C. DE C., *Fuel*, **7**, 452 (1928).



This phenomenon has been clarified especially by H. Schulze (Fig. 105) by means of (unpublished) slow-motion photographs—1200 pictures per second. The pictures show that, with the fresh gas streaming toward it, whole sections of unburned gas can also get behind the flame front, where they then burn. This can be seen on ordinary pictures of flames—on moving-picture film—in the form of shining streaks frequently observed but never explained that move in the opposite direction from the flame front.

The movement in the fresh gas during the progress of the flame can be seen especially clearly in experiments by Ellis,<sup>1</sup> who ignited the gas in a closed tube and a short time after ignition had another spark introduced at a different place. The movement of the second flame shows the gas currents caused by the first.



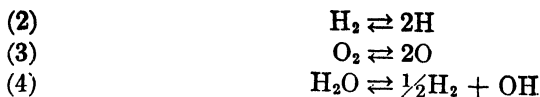
FIG. 105.—Flame movement in benzol-air mixtures (20 per cent super-rich) in a tube 5 cm in diameter (of which 4 cm were exposed for photographing). Taken with Thun's high-speed camera (1240 frames/sec). After the initial stages a "tipping" of the flame front takes place; on the inside of the tube a strong flow directed against the flame; corresponding flame form (like a Bunsen cone burning downward). The luminous spots visible at lower right might be due to the combustion of fresh gas that has been conducted behind the flame front by this gas current. (Courtesy of Mr. H. Schulze, Benzol Association.)

**2. Rate of Increase in Pressure and Flame Velocity.**—Even though it is possible to register the progress of explosions in closed chambers photographically through windows, the more important method is the recording of pressure. Pressure recording is the usual method for observing the course of combustion in internal-combustion engines. It is further absolutely necessary in the use of bomb explosions for determining the specific heats of gases, by which, from the recorded maximum pressure, the maximum temperature is computed. From this, given the heat of the reaction, the average specific heats of the reaction products between room temperature and reaction temperature are computed. In the computation, attention should be paid to the fact that the conversion will in general be incomplete on account of reaching an equilibrium and that in addition the reaction products can be dissociated. In the oxygen-hydrogen explosion, for example,



an equilibrium will be reached, according to 1; but  $\text{H}_2$ ,  $\text{O}_2$ , and  $\text{H}_2\text{O}$  are partly dissociated according to

<sup>1</sup> ELLIS, O.C. DE C., *Fuel*, 7, 452 (1928).



It is not possible to determine all these entities from a single explosion. It will therefore be necessary to draw upon other facts gained by experience, which we shall discuss at greater length when treating the computation of maximum flame temperatures (*cf.* pages 224*ff.*). Since the explosion method has been applied practically at only a few places to determine specific heat, the important problem for wider circles is precisely the reverse—to compute the maximum temperature of the maximum pressure from known data on specific heat, heat of reaction, and equilibria of dissociation. Moreover, this should take place under prescribed external conditions—at constant volume in the case of bomb explosions, at constant pressure in the case of free-burning flames, and with varying volume in some cases for the conditions of the working stroke of an internal-combustion engine.

Space prevents a detailed consideration of pressure indicators used with engines. For bomb explosions, suitable forms of membrane manometers are generally employed in which a light beam is deflected by the deflection of the membrane and thrown upon a mirror connected with the membrane. As far as the experimental technique for bomb explosions is concerned, especially the measurement of the pressure, we can only refer the reader to the original works.<sup>1</sup> For the purpose of recording pressure without inertia, the piezoelectric method employing quartz crystals is gaining in importance.<sup>2</sup>

Pressure measurements of course also show the time factor of an explosion in a closed chamber. It is possible also to draw conclusions as to average flame velocity from the total time of the explosions as well as to deduce the flame velocity at any moment from the rate of the pressure rise. We shall here derive the formulas necessary for approximate estimates. Let us take a spherical bomb of the radius  $R_0$ . Let it be ignited in the center at the time  $t = 0$ . Let the initial pressure be  $p_0$ , the maximum pressure at complete combustion  $p_c$ ; and, up to a certain point of time  $t$ , in which the portion  $\alpha$  of the entire gas has exploded, let the pressure  $p$  prevail. The most reasonable and at the same time simplest equation is to make the relative rise in pressure  $(p - p_0)/(p_c - p_0)$

<sup>1</sup> PIER, M., *Z. physik. Chem.*, **62**, 385 (1908). *Z. Elektrochem.*, **15**, 536 (1909). WOHL, K., and G. v. ELBE, *Z. physik. Chem.*, Sec. B, **5**, 241 (1929). WOHL, K., and M. MAGAT, *Z. physik. Chem.*, Sec. B, **19**, 536 (1932). LEWIS, B., and G. v. ELBE, *J. Am. Chem. Soc.*, **55**, 504 (1933); *cf.* especially "Combustion, Flames and Explosions of Gases." *Cf.* also the monographs by Bone, Newitt, and Townend.

<sup>2</sup> KLUGE, J., and H.E. LINKH, *Z. Ver. deut. Ing.*, **73**, 1311 (1929); **74**, 887 (1930); *Forsch. Gebiete Ingenieurw.*, **2**, 153 (1931); *Z. Instrumentenk.*, **52**, 177 (1932); *Forsch. Gebiete Ingenieurw.*, **4**, 177 (1933).

proportional to the relative conversion  $\alpha$

$$\alpha = \frac{p - p_0}{p_e - p_0} \quad (1)$$

This equation would be valid, for example, if the conversion were equally distributed over the entire volume and if the specific heats did not depend on the temperature. In reality, this is not the case, and thus (1) can be only an approximation. It will be shown later, however, that, by means of reasonable omissions and a stricter calculation, it is possible to return to (1). We can therefore employ this equation for an analysis of the combustion process in bombs for the time being without hesitation.

If a pressure-time curve of a bomb explosion takes the course shown in Fig. 106, it follows that the mass conversion velocity increases as the explosion progresses.

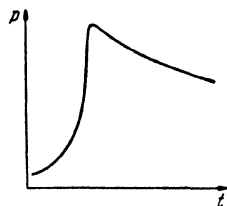


FIG. 106.

This is due in great part to the increase in area of the burning surface. In order to find the actual burning velocity, we must compute the position of the burning surface using the pressure, the degree of conversion  $\alpha$ , and the known dimensions of the bomb (radius  $R_0$ ). For this purpose, we proceed in the following manner, according to Lewis and v. Elbe.<sup>1</sup> Before combustion, let the portion  $\alpha$  of the gas have been within the sphere with the radius  $R_0$ ; then there was

$$\left(\frac{r_0}{R_0}\right)^3 = \alpha \quad (2)$$

and with (1)

$$\left(\frac{r_0}{R_0}\right) = \left[\frac{(p - p_0)}{(p_e - p_0)}\right]^{1/3} \quad (3)$$

The radius  $r_e$  of the sphere that takes in the same gas mass is obtained as the difference of the entire volume of the sphere and of the portion still unburned at the time  $t$  is obtained from

$$\frac{4}{3} \pi r_e^3 = \frac{4}{3} \pi R_0^3 - \sum m_0^j (1 - \alpha) \frac{RT}{p} \quad (4)$$

In this, the second member to the right represents the volume of the unburned portion  $(1 - \alpha)$ . For if  $\sum m_0^j$  is the entire mol mass present at the beginning of the experiment<sup>2</sup> and  $T$  is the temperature of the unburned gas at the time  $t$  (as a result of adiabatic compression by means of the progressing flame  $T > T_0$ , if  $T_0$  was the initial temperature; cf. page 137), the following is valid for the volume  $v$  according to the laws of gases.

$$pv = \sum m_0^j (1 - \alpha) RT$$

<sup>1</sup> LEWIS, B., and G. V. ELBE, *J. Chem. Phys.*, **2**, 283 (1934). Compare also "Combustion, Flames and Explosions of Gases," as well as FLOCK, E.F., and C.F. MARVIN, *Chem. Rev.*, **21**, 367 (1937).

<sup>2</sup>  $m_0^j$  is therefore the mol-number of the molecular type  $j$ .

(4) by means of (1) changes into

$$\frac{4}{3} \pi r_e^3 = \frac{4}{3} \pi R_0^3 - \sum m_0^i \frac{p_e - p}{p_e - p_0} \frac{RT}{p} \quad (5)$$

The entire volume  $\frac{4}{3} \pi R_0^3$  can be expressed likewise according to the laws of gases by the mol-number  $\sum m_0^i$  present in it at the temperature  $T_0$  and the pressure  $p_0$

$$\frac{4}{3} \pi R_0^3 = \frac{\sum m_0^i RT_0}{p_0}$$

with (5) after division with  $\frac{4}{3} \pi R_0^3$  and raising to the one-third power becomes

$$\frac{r_e}{R_0} = \left( 1 - \frac{p_0}{p} \frac{p_e - p}{p_e - p_0} \frac{T}{T_0} \right) \quad (6)$$

On the right side, in addition to  $T$ , are only directly measured entities;  $T$  is the temperature that the fresh gas originally at  $T_0$  has taken, owing to adiabatic compression from  $p_0$  to  $p$ . Therefore

$$T = T_0 \left( \frac{p}{p_0} \right)^{\kappa-1/\kappa} \quad (7)$$

if  $\kappa = c_p/c_v$  is the relation of the specific heats of the fresh gas at constant pressure and constant volume. By employing (6) and (7), it is now possible to obtain  $r_e$  as a function of time from a measured pressure-time diagram.  $dr_e/dt$  would be the flame velocity in the bomb,  $v_f$ . The normal combustion velocity  $v_n$  is obtained from this in the following manner. According to (2) or (3), we can directly obtain the radius  $r_0$  of the sphere that was occupied at the beginning of the experiment by the gas mass burned up to the time  $t$ , and we can obtain  $dr_0/dt$  from a diagram of  $r_0$  against  $t$ . This is for the time being only an arithmetical entity and gives the combustion velocity reduced to the volume at the beginning of the experiment. The volume of a spherical shell with the radius  $r_0$  and the thickness  $dr_0$  is

$$4\pi r_0^2 dr_0$$

In the moment in which this shell is reached by the flame, it is expanded to the greater value  $r_e$ , it has assumed the temperature  $T$ , and it is under the pressure  $p$ . Its volume is therefore now

$$4\pi r_0^2 dr_0 \frac{p_0}{p} \frac{T}{T_0}$$

In the time  $dt$ , the burning zone progresses toward the unburned gas mixture  $v_n dt$ . If we have chosen the thickness of the original gas layer so that the flame passes through it in the time  $dt$ , then clearly

$$4\pi r_e^2 v_n dt = 4\pi r_0^2 dr_0 \frac{p_0}{p} \frac{T}{T_0}$$

or

$$v_n = \frac{r_0^2}{r_e^2} \left( \frac{p_0}{p} \right)^{1/\kappa} \frac{dr_0}{dt} \quad (8)$$

in which we have substituted for  $T/T_0$  the value (7). The above equations suffice for the computation of  $v_n$  from recorded pressure-time curves. The method is of general applicability but has up to this time been used only by Lewis and v. Elbe<sup>1</sup> for the evaluation of ozone explosions.

<sup>1</sup> LEWIS, B., and G. v. ELBE, *J. Chem. Phys.*, **2**, 283 (1934).

Normal combustion velocities for ozone explosions (in the presence of oxygen) computed in this manner are given in Table 27.

TABLE 27

| $m^* = 3.05$ |               |                | $m = 1.5$   |               |                | $m = 1.02$  |               |                |
|--------------|---------------|----------------|-------------|---------------|----------------|-------------|---------------|----------------|
| $p$ , mm Hg  | $T^\circ$ abs | $v_n$ , cm/sec | $p$ , mm Hg | $T^\circ$ abs | $v_n$ , cm/sec | $p$ , mm Hg | $T^\circ$ abs | $v_n$ , cm/sec |
| 624          | 300           | 55             | 367         | 301           | 141            | 492         | 302           | 160            |
| 1353         | 301           | 100            | 1045        | 376           | 282            | 958         | 317           | 309            |
| 2499         | 427           | 158            | 2627        | 477           | 563            | 1469        | 411           | 615            |
|              |               |                |             |               |                | 4440        | 486           | 780            |

\*  $[\text{O}_2]/[\text{O}_3] = m$ .

It need hardly be mentioned that conversely in the same manner also the velocity of the pressure rise in a bomb explosion could be computed in advance, insofar as  $v_n$  were known as a function of initial pressure and temperature.

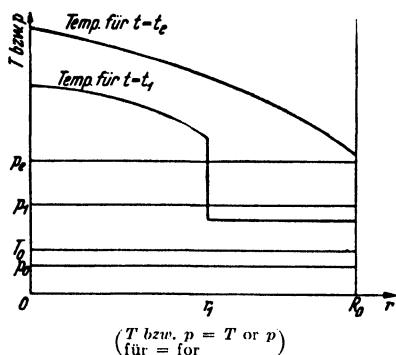


FIG. 107.— Variations in pressure and temperature during explosion in a spherical bomb, schematic. Compare the text. Indices 0, 1 and  $e$  at  $p$  and  $T$  refer to the beginning, a middle condition, and the end of the explosion.

as well as later. Further, there is graphed the position of the flame front, which is at  $r = 0$ ,  $r = r_1$ , and  $r = R_0$  for  $t = 0$ ,  $t = t_1$ , and  $t = t_e$  (end of the combustion), respectively. The pressure is constant over the entire chamber (the small changes in pressures that do exist can be completely ignored). The temperature is spatially constant in the unburned section but changes with the time. In the burned portion, it is not spatially constant. In the burning zone, it decreases suddenly. The

### 3. Theory of Pressure Increase and Temperature Gradient in Bomb Explosions, According to Mache.—

At this point, we should like to take up the more exact theory of the pressure increase in bomb explosions, which is to be sure elementary but somewhat intricate. We shall follow Mache<sup>1</sup> and Lewis and v. Elbe (cited page 119). First we shall call attention to Fig. 107 and recall the qualitative picture. In it are graphed pressure and temperature in the gas as a function of the radius  $r$  (bomb radius  $R_0$ ) at various times, namely, for the moment of ignition ( $t = 0$ )

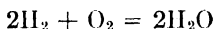
<sup>1</sup> MACHE, H., "Die Physik der Verbrennungserscheinungen." FLAMM, L., and H. MACHE, *Wien. Ber.*, **126**, 9 (1917).

specific volume is not plotted. This is a function of  $T$  and  $p$  (as well as the possible change in mol-number in conversion).

We must consider the changes in condition that appear in the combustion of a thin layer of gas (spherical shell) in the unburned as well as in the burned mixtures. The combustion of a thin layer whose volume is only a portion of the entire volume can be regarded as taking its course at practically constant pressure. During the combustion, the layer expands with a relation of terminal temperature to initial temperature multiplied by the "mol quotient"  $\mu$ , *i.e.*, the relation of the number of molecules of the terminal product to the number of those in the initial products of reaction.

$$\mu = \frac{\Sigma m_e^i}{\Sigma m_0^i} \quad (9)$$

where  $\Sigma m_0^i$  is the sum of the mol-numbers present before reaction, and  $\Sigma m_e^i$  is those present after the reaction. For example, in oxygen-hydrogen combustion (insofar as complete conversion results),



$\mu = \frac{2}{3}$ . By means of the expansion of the burning layer, the fresh gas as well as the burned gas is somewhat adiabatically compressed. Thus the condition of the fresh gas can easily be determined at any moment, since its initial condition was known and since everything is determined by the rise in pressure.

The situation is somewhat more complicated in the burned gas. Here every elementary layer is burned at a different initial temperature and a different initial pressure. Each was therefore also in a different initial condition when it was adiabatically compressed by the burning gases. A more detailed consideration is therefore required in determining the condition of the burned gases. We shall employ the terms as used above. In the bomb volume  $V = \frac{4\pi}{3} R_0^3$ , let  $\Sigma m_0^i$  mols of initial material

be present. Let the initial pressure and temperature be  $p_0$  and  $T_0$ . With completed explosion, let the maximum pressure  $p_e$  be reached. The temperature of the unburned gas as well as its pressure at a certain time (independent of the place) will be designated by  $p$  and  $T$ , which of course are different from  $p_0$  and  $T_0$  except for the time  $t = 0$ .

If a layer of gas that was at  $p$ ,  $T$  burns,  $p$  (up to magnitudes of a higher order) remains unchanged;  $T$  rises to a value  $\Theta$ , corresponding to the liberated heat of reaction and depending on the initial values  $p$ ,  $T$ , thus making it different for each layer at the moment of completed combustion.<sup>1</sup> In the burned layer of gas, pressure and temperature

<sup>1</sup>  $\Theta$  is thus to be computed from  $T$  at a heat of reaction assumed to be known. The process is to be regarded as proceeding under constant pressure.

continue to rise until the end of the combustion to the terminal value  $p_e$  independent of the place, and to a terminal value  $\Theta_e$ , which varies, like  $T$ , from layer to layer. In the following table, these terms are given once more.

|                    | Fresh gas                              |               | Burned gases                           |               |
|--------------------|--|---------------|--|---------------|
| Time.....          | $t = 0$                                | $0 < t < t_e$ | $0 < t < t_e$                          | $t = t_e$     |
| Pressure.....      | $p_0$                                  | $p$           | $p$                                    | $p_e$         |
| Temperature.....   | $T_0$                                  | $T$           | $\Theta(r)$                            | $\Theta_e(r)$ |
| Specific heat..... | $c_p^0, c_v^0, \kappa_0 = c_p^0/c_v^0$ |               | $c_p^e, c_v^e, \kappa_e = c_p^e/c_v^e$ |               |

The entities designated with Greek characters (except  $\kappa$ ) are still functions of the distance from the center of the sphere; the others are spatially constant. Since the condition  $p$ ,  $T$  of the fresh gas arises by means of adiabatic compression from the condition  $p_0$ ,  $T_0$ , the following is valid if  $v$  and  $v_0$  are the corresponding volumes:

$$p_0 v_0^{\kappa_0} = p v^{\kappa_0} \quad \text{or} \quad p_0^{\frac{1-\kappa_0}{\kappa_0}} R T_0 = p^{\frac{1-\kappa_0}{\kappa_0}} R T = F_0 \quad (10)$$

in which  $F_0$  is only an abbreviation for the expression (10). Applied to the burned gas, an analogous adiabatic relation is obtained.

$$\mu p^{\frac{1-\kappa_e}{\kappa_e}} R \Theta = \Phi(r) \quad (11)$$

In this, the factor  $\mu$  appears at the left because the mol-number in this relation has been changed. As has been explained above, however, we can apply no general expression here since the initial condition is different from layer to layer. For that reason, the expression on the left side of (11) is not a constant but changes from layer to layer.  $\Phi(r)$  is still a function of  $r$ .

For an exact calculation, we should now take into account the fact that the reaction does not generally take a complete course and that the reaction products are partly dissociated; further, that the specific heats and thus also  $\kappa = c_p/c_v$  are not independent of the temperature.<sup>1</sup> In order to avoid complicating the derivations too much, we shall first disregard dissociation. Secondly we shall, to be sure, not regard the specific heats as completely constant, but we shall assume for the fresh gas and for the burned gas in the temperature interval considered a constant average value for  $c_p$  and for  $c_v$ . By the choice of suitable average values, an error introduced in this manner could be kept quite small.

<sup>1</sup> By employing a numerical procedure, this is easily taken account of; cf. Chap. XII.

We must now seek a further relation for the burned gases that permits us to determine  $\Phi$  in Eq. (11).

If  $c_v^0$  is the average specific heat per mol of burned gas, the following adiabatic compression heat (from  $T_0$  to  $T$ ) is conducted to it.

$$c_v^0(T - T_0) \quad (12)$$

The most central volume element at the point of ignition burns at the lowest possible combustion temperature  $\Theta_0$ . Every other gas layer that has been preheated by compression burns at a higher temperature  $\Theta$ . In this, the excess energy referred to the volume element in the center, if  $c_v^e$  is the average specific heat per mol of the burned gas (related to a mol of initial mixture), is

$$\mu c_v^e(\Theta - \Theta_0) \quad (13)$$

in which the factor  $\mu$  takes care of the change of the mol-number by conversion. Now the excess energy that the second volume element, burned at the initial temperature  $T$ , has over the first volume element is determined<sup>1</sup> by the heat of compression conducted to it before; in other words,

$$\mu c_r^e(\Theta - \Theta_0) = c_r^0(T - T_0) \quad (14)$$

To repeat once more: In this equation,  $T$  and  $\Theta$  are the temperatures, varying from concentric layer to layer, immediately before and after combustion.  $T_0$  and  $\Theta_0$  have fixed values. The first is the initial temperature, the second the combustion temperature of the very first layer to be computed from the initial temperature and heat of combustion. If Eq. (14) is changed around in such a way that only these fixed values appear on one side, the resulting expression for given initial conditions must be a constant whose value can be given as

$$\mu c_v^e \Theta_0 - c_r^0 T_0 = \mu c_v^e \Theta - c_r^0 T = K \quad (15')$$

<sup>1</sup> This equation is not entirely correct. For the same reason that we give, Lewis and v. Elbe put  $c_p$  instead of  $c_v$  in (12), (13), (14), and the succeeding equations, but this is not justifiable. Since no great error can occur if  $c_p$  is substituted for  $c_v$  in Eq. (14), we shall continue to use the substitution. Instead, therefore, of starting from (15'), we shall use the analogous form (15), which uses  $c_p$ . It will be found that the succeeding expressions will be more easily integrated [the transition from (26) to (26')] depends of course on the incidental values of the coefficients] and that an easy survey of the relations will result. If a more exact calculation is desired, it is, of course, necessary to relinquish the closed form and to treat the problem numerically by thinking of the gas in the bomb as being divided into a number of layers, for instance, for each of which an average value of the temperature before and after combustion is computed. If a sufficient number of layers is chosen, any of the entities of interest can be computed to any desired degree of exactness. It would be somewhat cumbersome to compute the combustion velocity, but it would at any rate be possible.



For the reasons given in footnote 1 (page 151), we give  $c_p$  instead of  $c_v$  in Eq. (15'), thus

$$\mu c_p^0 \Theta_0 - c_p^0 T_0 = \mu c_p^e \Theta - c_p^0 T = K \quad (15)$$

This equation is to be regarded as an approximation.

By means of this relation, we shall now obtain the function  $\Phi$  from (11). By inserting (10) and (11) into (15), one obtains

$$\mu c_p^e \frac{\Phi}{\mu p^{(1-\kappa_e)\kappa_e} R} - c_p^0 \frac{T_0}{p^{(1-\kappa_0)\kappa_0} R} = K \quad (16)$$

and with

$$\frac{c_p}{R} - \frac{c_p}{c_p - c_e} = \frac{\kappa}{\kappa - 1}$$

this becomes

$$\frac{\kappa_e}{\kappa_e - 1} \Phi p^{(\kappa_e - 1)/\kappa_e} - \frac{\kappa_0}{\kappa_0 - 1} T_0 p^{(\kappa_0 - 1)/\kappa_0} - K = 0 \quad (17)$$

and from this

$$\Phi = \left[ K + \frac{\kappa_0}{\kappa_0 - 1} p^{(\kappa_0 - 1)/\kappa_0} T_0 \right] \frac{\kappa_e - 1}{\kappa_e} p^{(1-\kappa_e)/\kappa_e} \quad (18)$$

We are now interested in the condition of the burned gas at a definite spot or for a volume element that is burned after a known portion  $\alpha$  has been converted. So far this spot is characterized only by the pressure  $p$  that prevailed at combustion. We obtain a relation between  $p$  and  $\alpha$  if we impose the condition that the total volume must remain constantly equal to the volume of the bomb even though the volumes of the fresh gas and the burned gases change. For the total volume, we can, to begin with, apply the equation of ideal gases (page 146)

$$p_0 V = \Sigma m_0^i R T_0 \quad (19)$$

If the portion  $\alpha$  of the total gas is burned, and if  $T$  is the temperature of the fresh gas at the pressure  $p$ , there is valid for the volume of the fresh gas  $V_{(1-\alpha)}$

$$p V_{(1-\alpha)} = \Sigma m_0^i (1 - \alpha) R T \quad (20)$$

For an element  $d\alpha$  of the burned gas, the gas equation is likewise valid.

$$p dV = \Sigma m_e^i d\alpha R \Theta \quad (21)$$

Since  $\Theta$  changes from element to element, the entire volume of the burned gases can be obtained only by integration over the ranges of variable temperature at

$$V_\alpha = \sum m_e^i \frac{R}{p} \int_0^\alpha \Theta d\alpha \quad (22)$$

and the condition for the constancy of the total volume

$$V_{(1-\alpha)} + V_\alpha = V$$

becomes

$$\sum m_0^i \frac{R T_0}{p_0} = \sum m_0^i (1 - \alpha) \frac{R T}{p} + \sum m_e^i \frac{R}{p} \int_0^\alpha \Theta d\alpha \quad (23)$$

Since we do not have at our command an explicit relation between  $\Theta$  and  $\alpha$ , this expression is not very convenient. The temperatures  $T$  and  $\Theta$ , which go into (23),

can be expressed by (10) and (11), and we obtain

$$\int_0^\alpha \Phi d\alpha = \frac{RT_0}{p_0} p^{1/\kappa_0} - F_0 p^{1/\kappa_0 - 1/\kappa_0(1-\alpha)} \quad (24)$$

From this equation, we obtain by differentiation for  $\alpha$

$$\Phi = F_0 p^{\frac{1}{\kappa_0} - \frac{1}{\kappa_0}} + \left[ \frac{RT_0}{p_0} \frac{1}{\kappa_0} p^{\frac{1}{\kappa_0} - \frac{1}{\kappa_0}} - F_0 \left( \frac{1}{\kappa_0} - \frac{1}{\kappa_0} \right) p^{\left( \frac{1}{\kappa_0} - \frac{1}{\kappa_0} - 1 \right)} (1 - \alpha) \right] \frac{dp}{d\alpha} \quad (25)$$

If we insert the value of  $\Phi$  from (18), we have a differential equation for the degree of conversion  $\alpha$  as a function of the momentary pressure  $p$

$$K(\kappa_0 - 1) = \frac{\kappa_0 - \kappa_0}{\kappa_0 - 1} F_0 p^{(\kappa_0 - 1)/\kappa_0} + \left[ \frac{RT_0}{p_0} \frac{\kappa_0 - \kappa_0}{\kappa_0} F_0 p^{-1/\kappa_0} (1 - \alpha) \right] \frac{dp}{d\alpha} \quad (26)$$

Since

$$\frac{\kappa_0 - \kappa_0}{\kappa_0} p^{-\frac{1}{\kappa_0}} \frac{dp}{d\alpha} = \frac{d}{d\alpha} \left( \frac{\kappa_0 - \kappa_0}{\kappa_0 - 1} p^{\frac{\kappa_0 - 1}{\kappa_0}} \right)$$

(26) can be converted into

$$K(\kappa_0 - 1) = \frac{RT_0}{p_0} \frac{dp}{d\alpha} - \frac{d}{d\alpha} \left[ (1 - \alpha) \frac{\kappa_0 - \kappa_0}{\kappa_0 - 1} F_0 p^{\frac{\kappa_0 - 1}{\kappa_0}} \right] \quad (26')$$

which can be integrated without difficulty. If we integrate between the limits  $\alpha$  and 1 for  $\alpha$ , we obtain (taking into consideration that for  $\alpha = 1$  the pressure becomes  $p = p_0$ )

$$K(\kappa_0 - 1)(1 - \alpha) = \frac{RT_0}{p_0} (p_0 - p) + \frac{\kappa_0 - \kappa_0}{\kappa_0 - 1} F_0 (1 - \alpha) p^{(\kappa_0 - 1)/\kappa_0} \quad (27)$$

This equation represents with the above assumptions the exact relation between momentary pressure  $p$  and degree of conversion  $\alpha$ , solved according to  $(1 - \alpha)$ .

$$1 - \alpha = \frac{RT_0}{p_0} \frac{p_0 - p}{K(\kappa_0 - 1) - \frac{\kappa_0 - \kappa_0}{\kappa_0 - 1} F_0 p^{(\kappa_0 - 1)/\kappa_0}} \quad (28)$$

in which, according to (10),  $F_0 p^{(\kappa_0 - 1)/\kappa_0}$  is replaced by  $RT$ . If we introduce numerical values,<sup>1</sup> it is clear that  $\frac{\kappa_0 - \kappa_0}{\kappa_0 - 1} RT$  is always small in relation to  $K(\kappa_0 - 1)$ . We therefore make no great error in substituting  $T_0$  for  $T$ , otherwise Eq. (28) yields, for  $\alpha = 0$ ,

$$K(\kappa_0 - 1) = \frac{\kappa_0 - \kappa_0}{\kappa_0 - 1} RT_0 = RT_0 \frac{p_0 - p}{p_0} \quad (29)$$

If we substitute  $T_0$  for  $T$  and make use of (29), we obtain

$$1 - \alpha \cong \frac{p_0 - p}{p_0 - p_0} \quad \alpha \cong \frac{p - p_0}{p_0 - p_0} \quad (30)$$

<sup>1</sup>  $K$  is of the order of magnitude of the heat content of the burned gases, in other words mostly of the order of magnitude of about 10,000 cal/mol; the difference  $\kappa_0 - \kappa_0$  is of the order of magnitude 0.1,  $\frac{\kappa_0 - \kappa_0}{\kappa_0 - 1}$ , thus about 0.3; the member  $\frac{\kappa_0 - \kappa_0}{\kappa_0 - 1} RT$  is therefore about 100 to 300, i.e., small in proportion of  $K(\kappa_0 - 1)$ , even though not entirely negligible.

that is, the ultimate justification for the tentative relation for the degree of conversion as a function of the momentary pressure as it was employed above (page 145) in deriving the flame and combustion velocities.

The equations (28) and (29) can serve as the point of departure for the computation of any other desired entities. Equation (29) permits the direct computation of  $p_e$ , *i.e.*, of the maximum terminal pressure in explosion considering the temperature decrease in the gases. The numerical calculations of Lewis and v. Elbe have shown that the difference between  $p_e$  thus computed and the value resulting from that for uniform temperature distribution amounts in general to less than 1 per cent. Normally, therefore, the simpler calculation suffices. For the practical execution of the more accurate calculation of bomb explosions, we refer the reader to the works of Lewis and v. Elbe.

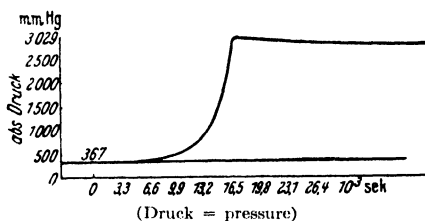


Fig. 108a.—Recording curve of a bomb explosion. Ozone explosion at 301° abs and 367 mm initial pressure; 40 per cent ozone in oxygen. (From Lewis and v. Elbe, "Combustion.")

As an example, we give the recorded curve of a bomb explosion in Fig. 108a, and in Fig. 108b the calculations according to Lewis and v. Elbe.

According to the adiabatic curve (10), we compute the temperature  $T$  of the unburned gas for the pressure of the moment  $p$ ; Eq. (28) permits a computation of the pertinent degree of conversion, or, more simply, Eq. (30). The temperature reached at every moment of the combustion can be computed from  $T$  with the usual relations. The value of  $\Theta_e$  at the end of the combination varying from mass element to mass element is computed from (11) with (18); (18) gives us the entity  $\Phi$  for the gas layer that burns at the pressure  $p$ . For this layer, Eq. 11 furnishes the temperature for any other pressure after the numerical value of  $\Phi$  has been inserted and therefore also for the pressure  $p = p_e$ , which prevails at completed combustion. The spatial position of the layer burning at the pressure  $p$  can be obtained by means of Eq. (30), which connects the momentary pressure with the degree of conversion. From this is obtained the position that the layer occupied before ignition. Since a temperature rise prevails toward the interior, the layer that was between the radii  $r_0$  and  $r_0 - dr_0$  at the beginning has shifted to a larger radius, a shift that disappears only at the limits of the sphere. If  $r_e$  is the radius of the surface of the sphere bounding the layer in

question after the experiment and  $r_0$  is the corresponding value of the beginning, a computation of  $r_e/r_0$  is possible by means of the methods described above. It is possible to achieve the same results more simply by imagining the gas before the experiment as being divided into a number of layers like  $n$ -layers of the thickness  $R/n$ . If  $v_0$  is the mol-volume

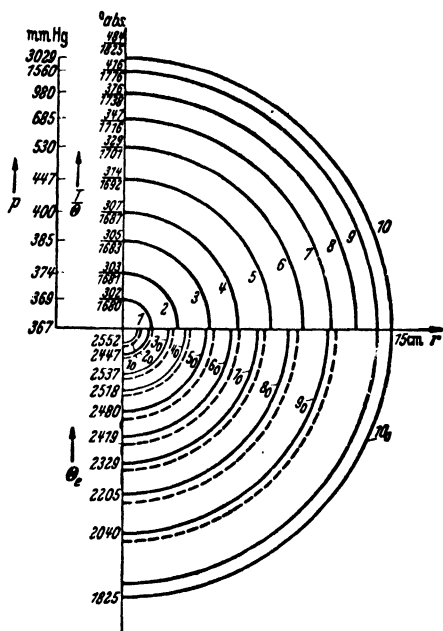


FIG. 108b.—Application of the recording curve 108a. Explosion in a sphere 15 cm in diameter. The circles 1, 2, . . . in the upper quadrant give the position of the flame front according to  $\frac{1}{2}t_{10}$ ,  $\frac{2}{2}t_{10}$ , . . . of the total duration of the explosion. For every position of the front, the corresponding pressures as well as the values of the temperature of the unburned gas ( $T$ ) and of the burned gas ( $\theta$ ) which are valid there, are given on the ordinate. The drawn circles 1a, 2a, . . . in the lower quadrant indicate the limits which the gas designated by the flame fronts 1, 2, . . . had assumed before combustion; the dashed circles represent the limits valid for the same volumes of gas at completed combustion. (From Lewis and v. Elbe, p. 144.)

before the experiment, at  $T_0$  and  $p_0$ , the volume  $v_e$ —assuming the ideal laws of gases—for the terminal pressure  $p_e$  and the average temperature  $\theta_e$  varying from layer to layer amounts to

$$\frac{v_e}{v_0} = \frac{\bar{\theta}_e}{T_0} \frac{p_0}{p_e} \mu$$

For further computations, cf. Lewis and v. Elbe (page 146).<sup>1</sup>

A direct computation of bomb explosions for the determination of

<sup>1</sup> Cf. in this connection also ENDRES, W., "Der Verbrennungsvorgang im Gas- und Vergasermotor," Julius Springer, Berlin, 1928.

flame velocities has, except for the example given, not yet been made;<sup>1</sup> but the velocity of the entire rise in pressure as a relative measure of the average flame velocity is in itself interesting enough to warrant a brief discussion of the experiments relating to it. Extensive material, especially on explosions at high initial pressures, has been assembled in both monographs by Bone<sup>2</sup> (included is material on experimental technique, on high-pressure bombs, and on manometers; *cf.* in this connection the original works quoted above).

**4. Specific Observations in Bomb Explosions.**—Facts regarding average flame velocities and their dependence on composition are furnished by a series of experiments by Fenning.<sup>3</sup> His work with mixtures of H<sub>2</sub>-air and carbon monoxide-air shows a decided dependence of the flame velocity on composition, a dependence shown also by carbon monoxide combustion at constant pressure. Table 28 shows that mix-

TABLE 28.—EXPLOSIONS OF H<sub>2</sub>-AIR + CO-AIR MIXTURES (FROM FENNING)  
Initial Temperature 50°C; Initial Pressure 5.2 atm

| Mixture               |          | Maximum pressure, atm | Time until reaching the maximum pressure, sec |   |
|-----------------------|----------|-----------------------|---|---|
| % H <sub>2</sub> -air | % CO-air |                       | From the passage of the spark                 | From the beginning of a perceptible rise in pressure on |
| 100                   | —        | 38.4                  | 0.0075  | 0.0059  |
| 49.7                  | 50.3     | 38.4                  | 0.0155  | 0.0123  |
| 24.8                  | 75.2     | 38.4                  | 0.0293  | 0.0239  |
| 11.9                  | 88.1     | 38.4                  | 0.0465  | 0.0383  |
| 8.0                   | 92.0     | 38.3                  | 0.0566  | 0.0482  |
| 4.1                   | 95.9     | 38.1                  | 0.0759  | 0.0645  |
| 2.2                   | 97.8     | 38.0                  | 0.1002  | 0.0860  |
| 0.2                   | 99.8     | 36.9                  | 0.2457  | 0.2048  |

The experiments were carried out in a cylindrical bomb about 18 cm in diameter and 20 cm in length; ignition in the center.

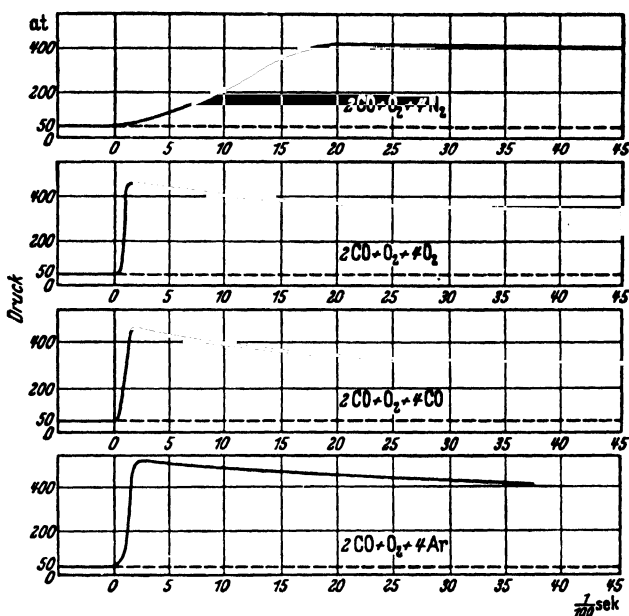
tures poor in hydrogen burn extraordinarily much more slowly than those rich in hydrogen. It can also be seen that, from the time of the spark to that of the perceptible rise in pressure, there is always a noticeable pause, an "ignition lag." To be sure, it is necessary to be very cautious in judging whether a time of that nature has elapsed between the spark

<sup>1</sup> For the method, see also E. Flock, and C.F. Martin, *Chem. Rev.*, **21**, 367 (1937).

<sup>2</sup> BONE, W.A., and D.T.A. TOWNEND, "Flame and Combustion in Gases," London, 1927. BONE, NEWITT, and TOWNEND, "Gaseous Combustion at High Pressures," London, 1929. Also BONE, NEWITT, and TOWNEND, *Proc. Roy. Soc. London*, A, **139**, 57 (1933). TOWNEND and L.E. OUTRIDGE, *Proc. Roy. Soc. London*, A, **139**, 74 (1933). NEWITT and F.G. LAMONT, *Proc. Roy. Soc. London*, A, **139**, 83 (1933).

<sup>3</sup> FENNING, *Rep. a. mem. aeron. res. committee*, quoted by Bone and Townend.

and the beginning of the flame propagation. Flame photographs show that such ignition lags actually can occur; but from the velocity of the pressure rise it cannot be concluded with certainty whether such is the case. In the case of average ignition in a spherical bomb, for instance, the burning surface is proportional to the square of the radius of the range covered. The velocity of the pressure rise, assuming a constant flame velocity, will be about 100 times as large if the burning surface is a sphere of 10 cm radius as if it is a sphere of 1 cm radius. Thus the velocity of the pressure rise from the moment of ignition is at first extra-



(Druck = pressure)

FIG. 109.—Pressure-time curves of high-pressure explosions of various carbon monoxide mixtures. Compare the text. (From Bone-Townend, "Flame.")

ordinarily slow even for normal flame velocity and can therefore be below the sensitivity of the indicator for a considerable time.

Of interest in connection with the phenomena already discussed under carbon monoxide combustion (page 121) are bomb explosions at high initial pressure (50 atm) by Bone and associates (cited page 156). In Fig. 109, we reproduce results by Bone and Townend. Remarkable in these graphs is (1) the remarkably slow pressure rise in carbon monoxide-air mixtures, and (2) the curve for the decrease in pressure. Normally the latter is exponential, and this is also the case for all mixtures in which atmospheric nitrogen is replaced by oxygen, carbon monoxide, or argon. The carbon monoxide-air curve should probably be interpreted

as the continuation of an exothermic reaction after reaching the maximum pressure. The same is probably true of nitrogen activation and its resultant reactions discussed elsewhere (Chap. IX, B).

Of interest is the dependence of the time  $\tau$ , extending to the end of the explosion, on the initial pressure. For this dependence, we herewith furnish several comparable values for the mixtures  $2\text{CO} + \text{O}_2 + 4\text{CO}$  according to Bone, Newitt, and Townend. The time does not change very much in this pressure interval, and the dependence on pressure is quite irregular. The situation is different in mixtures with oxygen excess,  $2\text{CO} + \text{O}_2 + 4\text{O}_2$ :

|   |        |       |      |       |
|---|--------|-------|------|-------|
| Initial pressure $p_0$ , atm.....         | 3      | 10    | 50   | 75    |
| Time to end of explosion, $\tau$ sec..... | 0.0225 | 0.035 | 0.01 | 0.015 |

|   |      |       |      |       |
|---|------|-------|------|-------|
| Initial pressure $p_0$ , atm.....                     | 3    | 10    | 25   | 50    |
| Time until reaching maximum pressure, $\tau$ sec..... | 0.06 | 0.045 | 0.01 | 0.005 |

Here the flame velocity obviously increases greatly with rising pressure. The opposite is true of mixtures of  $2\text{CO} + \text{O}_2 + 4\text{N}_2$ :

|                   |      |      |      |      |      |
|-------------------|------|------|------|------|------|
| $p_0$ , atm.....  | 3    | 10   | 25   | 50   | 75   |
| $\tau$ , sec..... | 0.07 | 0.10 | 0.15 | 0.19 | 0.30 |

Up to higher pressures, this is true analogously, as can be seen from experiments carried out on a different bomb:

|                   |      |      |      |      |      |
|-------------------|------|------|------|------|------|
| $p_0$ , atm.....  | 75   | 100  | 125  | 150  | 175  |
| $\tau$ , sec..... | 0.32 | 0.40 | 0.47 | 0.53 | 0.56 |

These experiments thus tie in with the observation on combustion velocities at lower pressures (Chap. III, pages 89, 90). For further experimental data, we refer to the works of Bone and associates as well as those of Newitt and Townend<sup>1</sup> already quoted.

At the conclusion, we wish to point out several special phenomena. If a tube in which a flame is propagating is narrowed—the tube itself can be open—the result can be a considerable rise in the flame velocity.<sup>2</sup> The cause for this is to be found in gas movements. A ring that is in the way of a flame causes an accelerated tongue of flame to shoot through its opening and a greater volume of gas to burn in a very short time. Increases in velocity from 0.7 to 420 m/sec are noted.

<sup>1</sup> NEWITT, D.M., and D.T.A. TOWNEND, *Combustion Phenomena at High Pressures*, "The Science of Petroleum," Vol. IV, Oxford, 1938.

<sup>2</sup> KIRKBY, W.A., and R.V. WHEELER, *J. Chem. Soc.*, 1931, p. 2303, and earlier works.

In addition, gas oscillations<sup>1</sup> in closed tubes are noted that almost certainly cannot be regarded as a shock wave caused by a rapidly moving flame. They must rather be a matter of an amplification of oscillations according to the mechanism H. Schulze has suggested (page 143). In a very general form, the formal theory of such processes has been given recently by Gunderley.<sup>2</sup>

<sup>1</sup> NÄGEL, A., and associates, and NIELSEN, *Forsch. Gebiete Ingenieurw.*, (6), 4. KÖCHLING, A., *Z. Ver. deut. Ing.*, **82**, 1126 (1938).

<sup>2</sup> GUNDERLEY, G., Eigenschwingungen in brennenden Gasgemischen, *Z. angew. Math. Mech.*, **18**, 263 (1938).



## CHAPTER V

### DETONATION

**1. Special Phenomena in Very Rapid Flames. Detonation.**—Even though the laws that govern the propagation of flames are by no means known in detail, experiments as well as theoretical reflection show that the normal combustion velocity is essentially determined, among other things, by the velocity of the chemical reaction in the burning zone. The greater the reaction velocity, the greater is the flame velocity, other things being equal. It is interesting to speculate what takes place if the velocity of the chemical reaction is increased very much.<sup>1</sup> Obviously the flame velocity cannot increase to an unlimited degree, as might at first be assumed; for the reaction velocity is not the only entity that determines the flame velocity. On one hand, heat is conducted to the fresh gas from the burning zone; and, on the other hand, active particles diffuse into the fresh gas, and fresh gas diffuses into the burning zone. If one imagines the reaction velocity in the burning zone as increased beyond all bounds, then the drop in temperature gradient and concentration gradient in the burning zone could be arbitrarily great. Nevertheless, the heat flow and the diffusion flow will not be able to rise above a certain limit, for heat and material are transported by the movement of the molecules. Since, however, in a given heat production of the reaction even when the reaction velocity is arbitrarily accelerated, it is possible to attain only the same maximum temperature corresponding to that of an average molecular velocity of at the most several kilometers per second, then that is also the maximum velocity at which heat and active particles can be transported and to which the flame can approach no matter how much the reaction velocity may have been accelerated.

That the maximum propagation velocity of a flame can certainly be no greater can be demonstrated in another way. Let us imagine (Fig. 117*a*, page 172) that the combustible mixture is in a tube open at one end and that the burning surface is moving toward the closed end. Then the burned gas must flow off toward the open end of the tube with a velocity many times that of the flame velocity, since the volume of the hot burned gases is likewise many times that of the fresh gas. At normal combustion velocities of several meters per second, no special effects result. If one imagines a flame with a velocity of several kilometers per second progressing to the right, the burned gases would have to flow

<sup>1</sup> In this connection, *cf.* the last section of this chapter.

off to the left with a velocity several times as great, or tremendous differences of pressure would have to appear. The energy of the directed flow of the departing gases must naturally also be furnished by the heat of reaction, and the velocity with which the gases can stream out is therefore limited. The flame velocity is also limited by this. In addition, the following new problem appears. As long as the flame velocity was small, we hardly had to bother about the pressure drop that is present in the direction of the tube axis; but, if the burned gas is to withdraw with a velocity of several kilometers per second, a considerable drop in pressure is necessary and must likewise lead to a compression of the fresh gas ahead of the flame front. To put it concretely: The more rapidly the gases are to flow off, the greater must be the recoil they transmit to the fresh gas. Continuing—details will be discussed later—this compression of the fresh gas produces a shock wave that progresses with a velocity greater than sound, and the burning zone is coupled with the front of this wave. This process is called *detonation*. From the preceding, it is clear that the velocity of the detonation may not be greater than of the order of magnitude of the thermal velocity of the burned gases, *i.e.*, several kilometers per second.

A flame propagation that bears all the characteristics of detonation was discovered in 1881 by Berthelot and Vieille as well as by Mallard and Le Chatelier.<sup>1</sup> The same authors made detailed studies of the same phenomena.<sup>2</sup> Soon thereafter, the study of detonation phenomena was taken up by Dixon,<sup>3</sup> whose students did most of the later English work in this field.

Among other methods, Mallard and Le Chatelier employed photography, which is generally used today. At that time, a movable plate was utilized instead of a film revolving on a drum. The chronoelectric method, used in their first experiment by Berthelot and Vieille, can still be used today in the measurement of detonation velocities, insofar as only the determination of the velocity at various stages comes into consideration and not other details of the detonation process. At certain definitely measured distances in the tube, probes are placed; in these, an electric contact is either broken by the passing of the detonation wave (penetration of tin foil in Berthelot and Vieille's experiment) or closed (jumping of a spark between two electrodes that are so far from each other that a bridging of the gap is possible only in the hot ionized gases), and the closing or opening of the circuit is recorded.

<sup>1</sup> BERTHELOT, M., and P. VIEILLE, *Compt. rend.*, **93**, 18 (1881); **94**, 149, 822 (1882). MALLARD, E., and H.L. LE CHATELIER, *Compt. rend.*, **93**, 145 (1881).

<sup>2</sup> BERTHELOT, M., and P. VIEILLE, *Ann. chim. phys.*, **28**, 289 (1883). MALLARD, E., and H.L. LE CHATELIER, *Ann. mines*, (8), **4**, 274, 335 (1883).

<sup>3</sup> DIXON, H.B., *Phil. Trans. Roy. Soc. London, A*, **184**, 97 (1893); **200**, 315, (1903).

The first observations of detonation showed the following: If a mixture capable of detonation is ignited at the open end of a tube, a stage of the vibrations sometimes forms in the initially uniform, normal flame

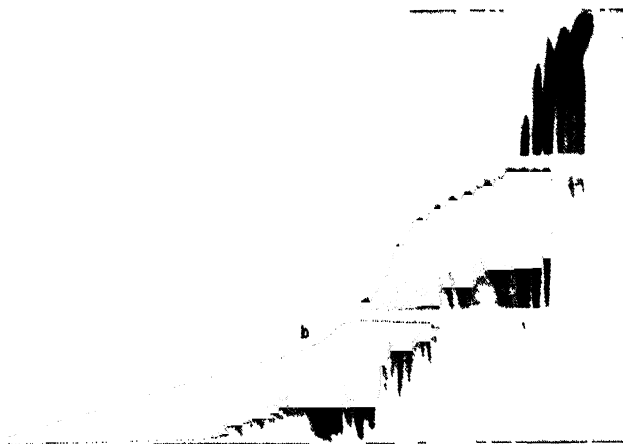


FIG. 110a.— $\text{CS}_2 + 6\text{NO}$  ignited at the open end of a tube 3 m long; from *a* to *b* normal flame, then oscillations. (From Mallard and Le Chatelier; taken from Bone-Townend, "Flame")

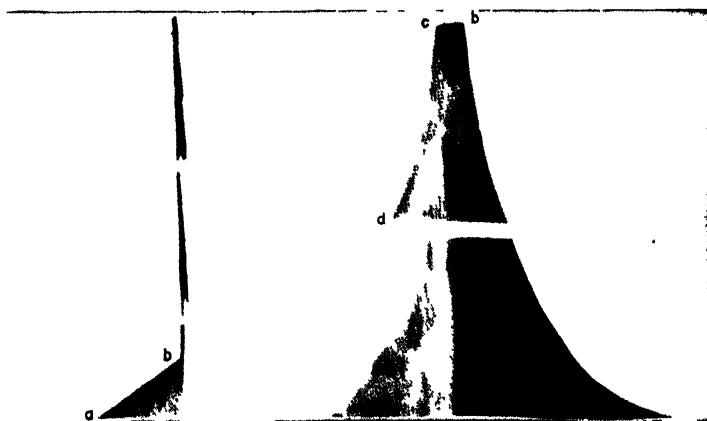


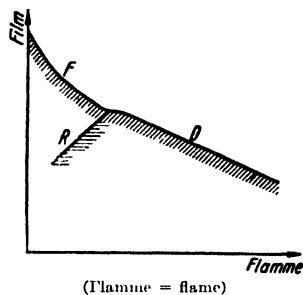
FIG. 110b.— $\text{CS}_2$ -oxygen ignited at the open end of the tube. At *b*, passing over into detonation. (From Mallard and Le Chatelier.)

FIG. 111.— $\text{CS}_2 + 6\text{NO}$ , ignited at the closed end of a tube 2 m long (at *a*); reversed flame in the burned gases. (From Mallard and Le Chatelier.)

velocity, which is then converted into detonation. However, an abrupt transition to detonation can also take place from the initially uniform flame velocity. The flame pictures obtained in this process by Mallard and Le Chatelier are shown in Fig. 110. With ignition at the closed end

of the tube, where the expanding combustion gases aid in accelerating the flame, there is a flame accelerated from the start which then finally goes over into detonation (Fig. 111). It was found that the detonation velocity is a characteristic constant for a given mixture. The value of this velocity is independent of the diameter of the tube in which the detonation is taking place, if this is not too small (7 mm is, for example, a sufficiently large diameter). Initial pressure and temperature have little influence on the velocity of the detonation. Changes in the composition of the mixture, on the other hand, exercise a considerable influence. All numerical values that have been found for the detonation velocity of gases lie between 1 and 4 km/sec.

A characteristic phenomenon connected with the appearance of detonation is that first observed by Dixon. At the place where the flame converts into detonation, there appears at the same time a wave that goes backward. It is designated by Dixon the "retonation wave" (Fig. 112), and its velocity, though smaller than that of the detonation wave, is of the same order of magnitude. Obviously this wave must appear because of the conservation of impulse. The impulse transmitted to the forward-directed detonation wave at the moment of its origin must be compensated for by the impulse given off to the retonation wave running in the opposite direction.



(Flame = flame)  
FIG. 112. Origin of a detonation  $D$  from a flame  $F$ , schematic. At the transition the "retonation" wave  $R$  appears.

It will aid in the comprehension of this discussion if we present an elementary theory of the detonation wave before going into experimental detail.

**2. Shock Wave and Detonation.**—For the theoretical explanation of the detonation phenomena, we are indebted to Chapman<sup>1</sup> and Jouguet.<sup>2</sup> A particularly detailed and systematic investigation of the percussion stroke has been given by Becker,<sup>3</sup> whom we shall follow in the succeeding discussion.

For a theoretical understanding, we must be clear about two things: (1) the origin of a shock wave, and (2) how chemical conversion can be

<sup>1</sup> CHAPMAN, D.L., *Phil. Mag.*, (5), **47**, 90 (1899).

<sup>2</sup> JOUGUET, E., *J. math.*, 1905, p. 347; 1906, p. 6; "Mécanique des explosifs," Paris, 1907, *Chaleur et ind.*, January, 1939.

<sup>3</sup> BECKER, R., *Z. Physik*, **8**, 321 (1922); *Z. Elektrochem.*, **42**, 457 (1936). Attention is also called to the work of E. Bollé; "Handbuch der physikalischen und technischen Mechanik," Vol. VI, Leipzig, 1927, as well as to the articles by R.P. Fraser, and by P.F. Laffitte, "The Science of Petroleum," Vol. IV, Oxford, 1938; and also to Lewis and v. Elbe, "Combustion, Flames and Explosions of Gases."

connected with the progress of the wave, how reaction energy maintains the shock wave, and how one can arrive at a quantitative computation of the detonation velocity from it. Let us imagine a gas (Fig. 113) in a tube one end of which is closed by a piston. Whether the other end is open or closed makes no difference. We now accelerate the piston, which at first was at rest, up to a constant final velocity, at which it then remains. A shock wave will form in the gas, *i.e.*, a compressed volume



FIG. 113.

of gas borders on the fresh gas at an unstable surface;<sup>1</sup> the unstable surface progresses toward the fresh gas with a velocity greater than sound.

How this takes place can be made clear, according to Becker, in the following manner. We again imagine the gas enclosed in a tube (Fig. 114) into which a piston is not continuously accelerated but rather moved from the point of time  $t = 0$  till  $t = \tau$  with the (small) constant velocity  $v_1$ . The gas in front of the piston will be a trifle compressed, and a pressure wave will move ahead of the piston with approximately the velocity of sound (it will move at exactly the velocity of sound if  $v_1$  is extremely small) (Fig. 114*a*). If from the time  $t = \tau$  the piston is allowed to move with the greater velocity  $v_2$ , a new pressure wave arises

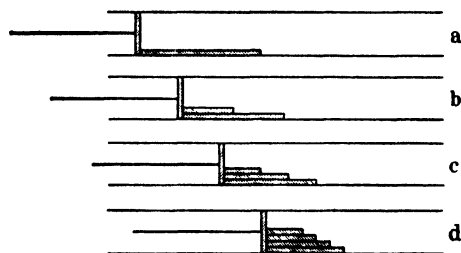


FIG. 114.—Origin of a percussion wave. (From Becker.)

(Fig. 114*b*) that moves somewhat faster than the first, since it moves in the gas that has already been heated somewhat by the foregoing compression and is flowing to the right with the velocity of the piston. Likewise, if we give the piston another increased velocity  $v_3$ , in the time  $2\tau$ , a third pressure wave will arise that will move more rapidly than the other two for the same reasons, etc. (Fig. 114*c* and *d*). Since each succeeding wave will move more rapidly than the preceding, the following waves must finally overtake the first one. A wave of infinitely steep front arises, *i.e.*, a shock wave or a detonating wave that moves with a velocity greater than sound, a velocity, indeed, that will increase as the compres-

<sup>1</sup> An unstable surface prevails only as long as the gas is considered a continuum, disregarding conduction and internal friction; otherwise there is a finite transitional layer, although it is very thin (*cf.* Becker).

sion in the wave increases.<sup>1</sup> It is to be expected that the velocity of the shock wave in order of magnitude will be approximately in the ratio of the velocity of the piston to the velocity of sound.

It is not difficult to compute, by means of elementary relations, the velocity of a stationary shock wave with the piston moving forward with constant velocity. Let us consider a system of coordinates moved along with the wave front (Fig. 115b). Figure 115a shows our former point of view. The piston and the previously compressed gas move to the right relative to the stationary tube with the velocity  $w$ ; the wave front correspondingly moves to the right with the velocity  $D > w$ . If we want to make the wave front stationary, we must move the tube with the fresh gas to the left with the velocity  $D$ .  $D$  is therefore the velocity with which the fresh gas streams toward the wave front for an observer moving along with the latter. Correspondingly the gases flow from the wave front with the velocity  $(D - w)$ . If, in a general way, we designate magnitudes characterizing the fresh gas with the index 1, and those concerning the compressed gas with the index 2, we can for the time being disregard the processes in the wave front and merely apply the laws for the conservation of mass, energy, and impulse to the gas before and behind the wave front.

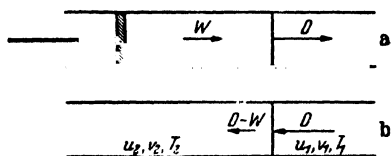


FIG. 115.

If we designate the velocity with  $u$ , the volume (of the mass unit, not of a mol) with  $v$ , hence the density with  $1/v = \rho$ , the pressure with  $p$ , and the internal energy per unit mass with  $E$ , we can put forward the following relations.  $u_1\rho_1$  is clearly the mass of the fresh gas flowing in a unit of time per unit of cross section. Since we are considering a stationary situation, this mass must be equal to the mass of the burned gases, in other words,  $u_2\rho_2$ . We thus obtain

$$u_1\rho_1 = u_2\rho_2 \quad \text{or} \quad \frac{u_1}{v_1} = \frac{u_2}{v_2} \quad \text{conservation of mass} \quad (1)$$

The impulse transported from the fresh gas as the result of its flow is per unit of mass  $u_1$ . Since the mass  $u_1/v_1$  (see above) flows in the unit of time, the impulse transported by it  $= u_1^2/v_1$ . However, the gas also transmits impulse as a result of its undirected molecular movement, namely, as a result of its hydrostatic pressure. In the kinetic gas computation of the pressure, use is made of the fact that  $p$  is the impulse transmitted per unit of cross section in the unit of time (see Chap. VIII).

<sup>1</sup> On the oscillations in air columns with a large amplitude, see C. Mayer-Schuchard, *Ver. deut. Ing. Forsch.*, No. 376 (1936).

Thus  $p_1$  is to be added to the above expression. Equating the corresponding expressions for fresh gas and burned gases leads to the equation

$$\frac{u_1^2}{v_1} + p_1 = \frac{u_2^2}{v_2} + p_2 \quad \text{conservation of impulse} \quad (2)$$

The energy equation leads to a third equation. The energy of the gas is composed of internal energy  $E$ , volume energy  $pv$ , and kinetic energy of the flow, which, referred to the unity of mass, equals  $u^2/2$ ; thus the energy principle yields

$$E_1 + \frac{u_1^2}{2} + p_1 v_1 = E_2 + \frac{u_2^2}{2} + p_2 v_2 \quad \text{conservation of energy} \quad (3)$$

From these equations, we obtain

$$u_1^2 = v_1^2 \frac{p_2 - p_1}{v_1 - v_2} \quad (4)$$

$$u_2^2 = v_2^2 \frac{p_2 - p_1}{v_1 - v_2} \quad (5)$$

$$E_2 - E_1 = \frac{1}{2}(p_1 + p_2)(v_1 - v_2) \quad \text{Hugoniot} \quad (6)$$

We shall discuss the latter equation in detail. It represents the connection between internal energy before and after compression by the shock wave as a function of the pressures and the specific volumes. The change in condition in the shock wave is, according to the meaning of the word, an adiabatic one, *i.e.*, no heat at all is exchanged with the surroundings; but Eq. (6) changes into the equation of the adiabatic (which would more correctly be termed isentropic)

$$dE = -p \, dv \quad (7)$$

which can be integrated in the well-known manner, only at a very small compression ratio and correspondingly small change in pressure. Then  $p$  can simply be written for  $(p_1 + p_2)/2$ , and  $-dv$  be substituted for  $(v_1 - v_2)$ . The change in condition of a shock wave is normally different from that for adiabatics. The gas in a shock wave is, we shall see, more strongly heated than one would expect in an adiabatic. How does this come about? We assume in deriving an adiabatic (and in all analogous calculations) that the change in condition takes place reversibly, *i.e.*, infinitely slowly, and that at any moment the pressure working on the piston from the outside is only a very little above the gas pressure. If we compress with finite velocity, a greater pressure than corresponds to the gas pressure of the moment must be exerted on the piston. Therefore more work will be needed for compression than is calculated by the adiabatic. We are generally not conscious of the infinitely slow change of condition when applying the adiabatic, since, in order to conduct a process adiabatically, we generally have it proceed as rapidly as possible.

It may be called to mind, however, that, in the usual examples for adiabatic application, the condition of a sufficiently low velocity is fulfilled, even for the oscillations of gas particles if it is a matter of the velocity of sound; for, even though the frequency of the sound waves can be high, the amplitudes with which the gas particles oscillate are so small that the velocities remain small compared with the molecular velocities, and upon this fact everything depends.

If we should apply the adiabatic for the change in condition in the shock wave as Riemann originally did<sup>1</sup> (he first recognized the possibility of shock waves from the mathematical point of view), we should conflict with the energy principle. The consistent application of the energy principle first led Hugoniot to Eq. (6), and it is now generally known by his name.<sup>2</sup> In the shock wave, as a result of rapid compression by the burned gases striking on the fresh gas with great kinetic energy of the directed movement, this fresh gas is sometimes heated to considerably higher temperatures than one would suppose from the compression relation.

Equations (4) to (6) permit a computation of the velocity of the shock wave as well as of the rise in temperature appearing in it if, in addition to the condition of the fresh gas ( $p_1, v_1, T_1$ ), either the compression-stroke pressure  $p_2$  is given or the compression relation ( $\epsilon = v_1/v_2$ ) or also the "velocity of the burned gases"  $w$ , which, according to Fig. 115b, is equal to  $u_1 - u_2$  or to the velocity<sup>3</sup> with which the piston is moved. Here, to be sure, the specific heat  $c_v$  of the gas mixture must be known in order to express  $E_2 - E_1$  as the function of the temperature

$$E_2 - E_1 = \int_{T_1}^{T_2} c_v dT \quad (8)$$

or

$$E_2 - E_1 = (T_2 - T_1)c_2 \quad (8a)$$

the latter if one is computing with an average value of the specific heat. Now we shall assume the validity of the ideal laws of gases for the gases in question

$$pv = R'T \quad (9)$$

Regarding the numerical value  $R'$ , it must be borne in mind that  $v$  stands for the volume of the mass unit, not that of the mol. Equations (9), (8), and (6) permit the calculation of  $T_2$  and  $v_2$  if  $p_2$  is given.

From this, the velocity of the shock wave can be obtained from (4)

$$u_1 = D = v_1 \sqrt{\frac{p_2 - p_1}{v_1 - v_2}} \quad (10)$$

and the velocity of the burned gases

$$w = u_1 - u_2 = (v_1 - v_2) \sqrt{\frac{p_2 - p_1}{v_1 - v_2}} \quad (11)$$

<sup>1</sup> RIEMANN, B., *Nachr. Ges. Wiss. Göttingen*, 8, 1860.

<sup>2</sup> HUGONIOT, *J. école polytech.*, Nos. 57 and 58, 1887, 1889.

<sup>3</sup> We are disregarding correction factors.



For very small values of  $(p_2 - p_1)$ , Eq. (10) changes into the usual equation for the velocity of sound (*cf.* page 203), just as Hugoniot's equation changes into the adiabatic.

To illustrate, we shall furnish in Table 29 (from R. Becker, cited page 163) numerical values for air at 273° abs initial temperature and various compression pressures  $(p_2/p_1)$ . Given are the compression ratio  $v_1/v_2$ , the terminal temperature  $T_2$  compared with the temperature that would be computed with adiabatic compression, the velocity  $D$  of the

TABLE 29.—SHOCK WAVES IN AIR AT 273° ABS. (FROM R. BECKER)

| $p_2/p_1$ | $v_1/v_2$ | $T_2$ , ° abs | $T_2$ (computed<br>from the<br>adiabatics),<br>° abs | $D$ , m/sec | $w$ , m/sec | $i/p_1$ |
|-----------|-----------|---------------|--|-------------|-------------|---------|
| 2         | 1.63      | 336           | 330  | 452         | 175         | 1.63    |
| 5         | 2.84      | 482           | 426  | 698         | 452         | 11.4    |
| 10        | 3.88      | 705           | 515  | 978         | 725         | 34.9    |
| 50        | 6.04      | 2,260         | 794  | 2,150       | 1,795       | 296     |
| 100       | 7.66      | 3,860         | 950  | 3,020       | 2,590       | 699     |
| 1,000     | 14.3      | 19,100        | 1,710  | 9,210       | 8,560       | 14,300  |
| 2,000     | 18.8      | 29,000        | 2,070  | 12,900      | 12,210      | 37,600  |

shock wave as well as  $w$  of the burned gases, and finally also the effective pressure of the shock wave. If a shock wave meets an obstruction, it has an effect not only by virtue of its hydrostatic superpressure  $(p_2 - p_1)$  but in addition by virtue of the impulse of the directed current. The impulse thus transmitted in a unit of time is (*cf.* page 168)

$$\frac{w^2}{v_2} = \frac{v_1 - v_2}{v_2} (p_2 - p_1)$$

employing (11). The total impulse of the shock wave thus becomes

$$i = p_2 - p_1 + (p_2 - p_1) \frac{v_1}{v_2} \frac{v_2}{v_2} = (p_2 - p_1) \frac{v_1}{v_2}$$

In the last column of the table, the relation  $i/p_1$  is given. In applying these results to detonation later, it must be remembered that the layer of burned gases that moves to the front with the velocity  $w$  is very thin. The high-pressure impulse is therefore effective for only a short time.

Becker's numerical values are somewhat antiquated today because they are based on the older values for specific heat, but this makes no difference in judging the relations. Compression pressures in detonations of gases at atmospheric pressure are not over  $\sim 50$  atm. It is possible to cause shock waves in air by the detonation of solid explosives with veloci-

ties up to about 10 km/sec, however, and this might be the only method, as Becker points out, for experimenting with gases at temperatures of ten thousands of degrees and pressures of the order of magnitude of 1000 atm. The most important fact to be gained from Table 29 is that temperatures attained in shock waves are considerably above the values computed according to the static adiabatic.

If we want to keep the shock wave stationary for experimental purposes, the piston, as we have already seen, must be moved forward with the constant velocity  $w$ . Now we wish to make clear how a stationary shock wave acts when the necessary supply of energy is furnished by a chemical reaction taking place in the wave front. Equations (4) and (5), which express the conservation of mass and of impulse, are obviously entirely unaffected thereby. Only in (6) must a term be added to take care of the heat of reaction. Obviously it must be thus: To the increase in internal energy  $E_2 - E_1$ , in addition to the Hugoniot compression  $\frac{1}{2}(p_1 - p_2)(v_1 - v_2)$ , there must be added also the amount of the heat of reaction  $Q$ . Instead of (6), we must write

$$E_2 - E_1 = \frac{1}{2}(p_1 + p_2)(v_1 - v_2) + Q \quad (12)$$

or again, with the introduction of the average specific heat  $c_v$ ,

$$\bar{c}_v(T_2 - T_1) - Q = \frac{1}{2}(p_1 + p_2)(v_1 - v_2) \quad (13)$$

Equations (10) and (11) for the "detonation" velocity  $D$  and the burned gas velocity  $w$  remain the same as before, except that, for determining the condition of the burned gases, (13) must be substituted for (6), the ideal law of gases<sup>1</sup> again being used for eliminating  $T$ .

Since, under the conditions of detonation, no definite compression pressure  $p_2$  or compression ratio  $v_1/v_2$  can be advanced, (13) offers no definite terminal condition to correspond to an advanced initial condition  $v_1, p_1$  but rather an unlimited variety of terminal conditions possible from the standpoint of energy which are expressed by the "Hugoniot-curve" shown in Fig. 116. The point  $A (v_1, p_1)$  represents the initial condition. It itself is not on the curve; for, since the finite heat of reaction  $Q$  is set free, the initial condition and all the possible terminal conditions are always separated by a finite distance from one another. If we want to compute detonation and burned-gas velocities by means of (10) and (11), we must know into what terminal condition  $p_2, v_2$  the gas will change. It seems as if an arbitrary number of values would be

<sup>1</sup> For the detonation of gases at normal initial pressures, the ideal laws of gases furnish sufficiently accurate values; however, the validity of the equation given above is not dependent on this. For the detonation of condensed explosives where the burned gases show an extraordinary thickness, other condition equations that are suitable will have to be employed.

possible on the curve and that as a result no definite value for the detonation velocity could be assigned in contrast to clear experimental findings. A more detailed consideration reveals, however, that this is not the case. Let us assume for the present that the point  $B$  with  $v_2$  and  $p_2$  is the terminal condition. Then the detonation velocity, according to (10), would be

$$D = v_1 \sqrt{\frac{p_2 - p_1}{v_1 - v_2}} = v_1 \sqrt{\tan \alpha} \quad (14)$$

as can be seen from Fig. 116. This relation shows us that the branch of the curve from  $G$  to  $F$  can have no real meaning, since along this section

$\tan \alpha$  would be negative and  $D$  accordingly imaginary. The section  $FL$  obviously corresponds not to detonation but rather to ordinary combustion, for here the volume increases toward the initial condition, and the pressure decreases. The ordinary flame must of necessity be included in the above considerations, which make use of only the principles of the conservation of impulse, mass, and energy.

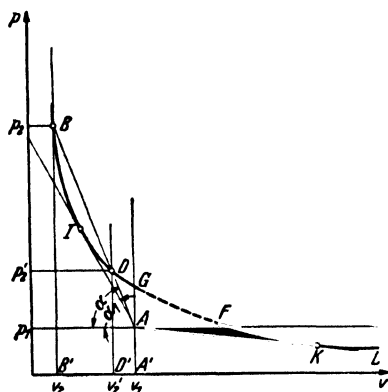


FIG. 116.—Hugoniot-curve; relations between  $p$  and  $v$  according to (13). The initial condition corresponds to the point  $A$ . (From R. Becker, p. 161.)

We thus need to consider only the section of the curve from  $G$  to  $B$  for detonation. Except at point  $I$ , at which the straight line from  $A$  forms a tangent to the Hugoniot-curve, there are always two conditions that belong to the same value of the detonation velocity, for example,  $D$  and  $B$ . It can be shown that the transition to  $D$  is unlikely and that on the other hand a detonation wave in which the terminal condition of the bases would correspond to the point  $B$  would not be stable. It would be overtaken and weakened by a rarefaction wave (which must always form some distance behind the front of the wave) until its velocity would have diminished to the smallest possible velocity, namely, that belonging to the transition toward  $I$ . At the terminal point  $I$ , the velocity of a sound wave in the burned gases plus the velocity of flow of the burned gases is exactly equal to the detonation velocity. The sound wave can therefore never overtake the detonation wave, and the latter is therefore stable. As a result, only a stationary detonation corresponds to the point  $I$ . More detailed reasons for the above will be given later when further theoretical considerations are discussed.

The point *I* (Fig. 116), as will be clear subsequently, is characterized by the fact that at it the Hugoniot-curve is touched by the adiabatic passing through *I*, in other words that

$$\tan \alpha_1 = \left( \frac{p_2 - p_1}{v_1 - v_2} \right)_I = - \left( \frac{dp_2}{dv_2} \right)_{ad} \quad (15)$$

or, since for the adiabatic

$$pv^\kappa = \text{const} \quad \frac{dp}{dv} = - \frac{\kappa p}{v}$$

$$\frac{p_2 - p_1}{v_1 - v_2} = \kappa_2 \frac{p_2}{v_2} \quad (16)$$

In (16),  $\kappa_2 = c_p/c_v$  is the ratio of the specific heat for the condition  $p_2, v_2, T_2$ . Equation (16) together with the former equations

$$D = v_1 \sqrt{\frac{p_2 - p_1}{v_1 - v_2}} \quad (10)$$

$$w = (v_1 - v_2) \sqrt{\frac{p_2 - p_1}{v_1 - v_2}} \quad (11)$$

and the Hugoniot-equation

$$\bar{c}_v(T_2 - T_1) - Q = \frac{1}{2}(p_1 + p_2)(v_1 - v_2) \quad (13)$$

use of the gas laws permits the computation of any desired entity. The last equation can be changed to  $p_1 v_1 = R_1 T_1$ ,  $p_2 v_2 = R_2 T_2^*$  and, by including the abbreviation  $\epsilon = v_1/v_2$  (compression ratio),

$$\bar{c}_v(T_2 - T_1) = \int_{T_1}^{T_2} c_v dT = Q + \frac{1}{2}(\epsilon - 1) \left( R_2 T_2 + \frac{R_1 T_1}{\epsilon} \right) \quad (17)$$

and, from (10) with (16),

$$D^2 = v_1^2 \kappa_2 \frac{p_2}{v_2} = \frac{v_1^2 \kappa_2 R_2 T_2}{v_2^2} = \epsilon^2 \kappa_2 R_2 T_2 \quad (10a)$$

and, from (16) after suitable conversion,

$$\kappa_2 \epsilon^2 - \epsilon(\kappa_2 + 1) + \frac{R_1 T_1}{R_2 T_2} = 0 \quad (16a)$$

The three equations (17), (10a), and (16a) suffice for computing the three unknowns  $T_2$ ,  $\epsilon = v_1/v_2$ , and  $D$ . Since  $\kappa_2$  is dependent on the temperature, the calculation must be made provisionally with an approximate value for  $\kappa$ , and by repetition the results for  $T_2$ ,  $p_2$ , and  $D$  are to be corrected. In this procedure, the  $\kappa_2$  belonging to the computed  $T_2$  is to be used for the next step (as is customary in computing combustion tempera-

\* As has already been noted (page 167), individual values of the gas constants must be introduced, since the computations refer to the mass unit and not to the mols. In practical calculation, it must be remembered that the mol-number often changes in conversion and also as the result of the dissociation of the end products.

tures). The calculation becomes considerably more involved if the dissociation of the end products must also be taken into account.

Wherever the theory has been tested by experience, the results have been such as to remove any doubt about the correctness of the basic assumptions. Graphically, the difference between ordinary combustion and detonation is as follows: In ordinary combustion, density and pressure of the burned gases are lower than in fresh gas; the burned gases flow back from the burning surface away from the fresh gas (Fig. 117a). In detonation, the burned gases flow toward the fresh gas (Fig. 117b) in the same direction in which the detonation progresses. In addition, the pressure in the burned gases is essentially higher than in the fresh gas.

From this, we cannot conclude, however, that the burned gases have the same forward velocity at any distance from the wave front. That

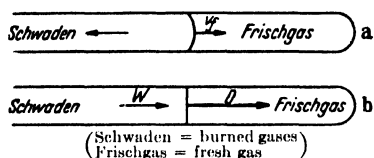


FIG. 117.—Progress of the burning zone and flow of the burned gases (with (a) ordinary flame, (b) detonation).

would be the case only if there were no decrease in pressure toward the rear, as, for example, by the insertion of a piston, as was discussed in the origin of shock waves. Normally, however, the pressure decreases toward the rear, and the direction of motion of the exhaust

gases reverses itself at some distance from the flame front. Therefore a rarefaction wave must always arise at some distance behind the wave front that follows the detonation. We thus see how important it is for the stability of the detonation wave that it cannot be overtaken by this rarefaction wave.

Langweiler<sup>1</sup> has expressed the detonation pressure  $p_2$  and the detonation temperature  $T_2$  in relation to the pressure  $p_0$  and the temperature  $T_0$ , which are attained by an explosion in a closed chamber. He gives

$$p_2 = 2p_0$$

and

$$T_2 = \frac{2\kappa}{\kappa + 1} T_0$$

These relations are not quite exact. The detonation pressure, for example, is a little less than  $2p_0$ , but they can be very useful for orientation. They can be derived from (16a) and (17) if certain factors are ignored. They cannot be exact, since the temperature dependence of the specific heats and of the dissociation of the combustion products are not taken into consideration in deriving them.

<sup>1</sup> LANGWEILER, H., *Z. tech. Physik*, **19**, 271 (1938).

Because detonation velocities can be computed only on the basis of thermodynamics and hydrodynamics, the following is always presupposed: The reaction velocity must always be so great that equilibrium is practically achieved in the wave front. If the conditions become too unfavorable for the reaction velocity (*e.g.*, in a fuel-oxygen mixture in the neighborhood of the burning zone) the mixture will not detonate at all. For given substances, detonation limits appear, and others are not able to detonate at all although they are explosive. Since there are never sudden transitions (in the sense that a mixture only a little beyond the limit would not detonate while another only a little this side of the limit would yield not only detonation but also the full detonation velocity), there is actually a continuous transition. In the immediate proximity of the limits, a process with the characteristic phenomena of detonation takes place, to be sure, but not with the full velocity; *i.e.*, the reaction velocity does not yet suffice for the complete appearance of equilibrium.

We shall come back later to basic questions in connection with the reaction velocity (pages 206ff.).

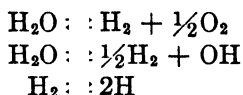
**3. Experimental Determination of Detonation Velocities.**—Berthelot was quite aware of the fact that the velocity of detonation must be of the order of magnitude of the thermal molecular velocity in the burned gases, and he attempted to make use of this fact in obtaining quantitative relations for the detonation velocity. As could be expected, there is a satisfactory agreement in point of order of magnitude, but it does not suffice in detail. Dixon has attempted to improve the results by similar means, but these attempts have only historical interest today.<sup>1</sup> Jouguet later computed<sup>2</sup> the detonation velocities for a large number of systems and found, with the measurement of Berthelot and Vieille, Le Chatelier and Dixon, an agreement with deviations that rarely go higher than 5 per cent. Since these computations are based on older values for specific heats and since at that time there was no accurate knowledge of the dissociation equilibria that are a determining factor in high temperatures, we shall omit the results here. In more recent times, B. Lewis<sup>3</sup> has attempted to compute detonation velocities in this manner with the aid of modern data.

In Tables 30 and 31, which follow, the results for oxygen-hydrogen explosion are given. In this case, the following dissociation equilibria at the high detonation temperatures must be taken into account:

<sup>1</sup> In Dixon [*Phil. Trans. Roy. Soc. London*, A, **184**, 152 (1893)], there is a note by A. Schuster that represents the first, if as yet unsatisfactory, application of Riemann's theory to detonation.

<sup>2</sup> Cf. the compilation in E. Bollé, in Auerbach-Hort, "Handbuch der physikalischen und technischen Mechanik," Vol. VI, p. 337, 1927.

<sup>3</sup> LEWIS, B., and FRIAUF, *J. Am. Chem. Soc.*, **52**, 3905 (1930).



Nothing fundamental is changed in the computation. When considering dissociation, it is necessary—as is usual in computing flame temperatures—to proceed by trial and error, a method that can be quite laborious in detail.

The numerical values of Table 30 are interesting from several points of view. For one thing, most of the theoretical values agree with the

TABLE 30—DETONATION VELOCITIES OF  $\text{H}_2\text{-O}_2\text{-N}_2$  MIXTURES ACCORDING TO EXPERIMENTS BY DIXON<sup>1</sup> AND PAYMAN AND WALLS,<sup>2</sup> AT 1 ATM OF INITIAL PRESSURE AND 291° ABS. WORKED OUT BY LEWIS AND FRIAUF (CITED P. 173)

| Mixture                                    | Detonation pressure, $p_2$ atm | Detonation temperature $T_2^0$ abs | Detonation velocity $D$ , m/sec |          | % content in the burned gas |      |
|--|--------------------------------|------------------------------------|---------------------------------|----------|-----------------------------|------|
|  |                                |                                    | Computed                        | Observed | OH                          | H    |
| $(2\text{H}_2 + \text{O}_2)$               | 18.05                          | 3583                               | 2806                            | 2819     | 25.3                        | 6.9  |
| $(2\text{H}_2 + \text{O}_2) + 1\text{O}_2$ | 17.4                           | 3390                               | 2302                            | 2314     | 28.5                        | 1.8  |
| $(2\text{H}_2 + \text{O}_2) + 3\text{O}_2$ | 15.3                           | 2970                               | 1925                            | 1922     | 13.5                        | 0.2  |
| $(2\text{H}_2 + \text{O}_2) + 5\text{O}_2$ | 14.13                          | 2620                               | 1732                            | 1700     | 6.3                         | 0.07 |
| $(2\text{H}_2 + \text{O}_2) + 1\text{N}_2$ | 17.37                          | 3367                               | 2378                            | 2407     | 14.7                        | 3.3  |
| $(2\text{H}_2 + \text{O}_2) + 3\text{N}_2$ | 15.63                          | 3003                               | 2033                            | 2055     | 5.5                         | 0.9  |
| $(2\text{H}_2 + \text{O}_2) + 5\text{N}_2$ | 14.39                          | 2685                               | 1850                            | 1822     | 2.1                         | 0.2  |
| $(2\text{H}_2 + \text{O}_2) + 2\text{H}_2$ | 17.25                          | 3314                               | 3354                            | 3273     | 5.9                         | 6.5  |
| $(2\text{H}_2 + \text{O}_2) + 4\text{H}_2$ | 15.97                          | 2976                               | 3627                            | 3527     | 1.2                         | 3.0  |
| $(2\text{H}_2 + \text{O}_2) + 6\text{H}_2$ | 14.18                          | 2650                               | 3749                            | 3532     | 0.3                         | 1.1  |

<sup>1</sup> DIXON, H.B., *Phil. Trans. Roy. Soc. London, A*, **184**, 97 (1893).

<sup>2</sup> PAYMAN, W., and WALLS, J. *Chem. Soc.*, 1923, p. 420.

experimental values to within 1 per cent, which is an extraordinary confirmation of the theoretical picture. However, there are also variations lying far beyond the limits of error, particularly in the case of especially rapid detonations. We have already pointed out (page 172) that the presupposition for detonation is a sufficiently high reaction velocity in the flame front. If this condition is fulfilled, the hydrodynamic theory permits an exact prediction of the detonation velocity. It is entirely conceivable that in some mixtures the reaction velocity is still great enough for the maintenance of a shock wave but not great enough for complete conversion in the burning zone. In this case, the actual conversion (not determinable in detail) in the proximity of the wave front would have to be taken into account, and a lower detonation

velocity would result. This is to be expected near the detonation limits (cf. pages 173, 181ff.) as well as in the case of especially high detonation velocities when a correspondingly high reaction velocity is presupposed. It is therefore not very surprising if, in the case of the highest detonation velocities, variations appear in the sense that the detonation velocity actually found is smaller than that computed for complete conversion in the wave front.

Another possibility of interpretation is to be considered, although up to the present there is no sure evidence for it. It is known from experiments especially by Eucken<sup>1</sup> and his associates that the exchange between the oscillation energy of multiatomic molecules and the kinetic energy of the movement of the center of gravity frequently takes place quite slowly. Under certain circumstances, molecular impacts of the order of magnitude up to  $10^5$  might be necessary for equalization. This is known from measurements of the dispersion of the velocity of sound where anomalies appear at high frequencies if the equalization between translation energy and oscillation energy is not rapid enough. The energy of reaction in the burning zone is largely liberated step by step, as in the case of  $\text{H} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O} + \text{M}$ , where one molecule of a triple collision M absorbs a part of the energy but where a large amount can still be present as the oscillation energy of the newly formed  $\text{H}_2\text{O}$  molecule. It is assumed for purposes of calculation, however, that the burned gas has a very definite temperature  $T_2$  that can be computed from the heat of reaction. This means that Maxwell-Boltzmann's velocity or energy distribution prevails. If this distribution cannot take place in the short available time, deviations between the observed and the calculated detonation velocity can result.<sup>2</sup> Two things must be differentiated: In the relatively thin layer of reaction, Maxwell's distribution will never exactly take place in the very brief available time (if we assume the layer of reaction of the order of magnitude of 10 free paths of travel,  $\sim 10^{-4}$  cm, then times of only  $\sim 10^{-9}$  sec would be available; in thicker layers, they would be correspondingly longer but even so quite short). But, if the deviation in the successive layers is on the average only 0, everything is satisfactory. As a result of the influences mentioned, a systematic, one-sided deviation from Maxwell's distribution is conceivable, perhaps in the sense that the kinetic energy of translation and thus the detonation velocity are smaller than those computed. From the fact that in many cases, assuming sufficiently rapidly reacting mixtures, the computed and the observed velocity coincide, it is to be concluded that in general the distribution of the energy over the various

<sup>1</sup> EUCKEN, A., cited p. 142.

<sup>2</sup> This possibility was pointed out some time ago by W. Jost, *Z. elektrochem.*, **41**, 183 (1935).



degrees of freedom under the conditions of detonation proceeds very rapidly, and the observed deviations near the detonation limits and in other cases will therefore be attributed rather to too low a reaction velocity.

The numerical values of the relative concentration of H and OH in Table 30 show, on the one hand, that by neglecting dissociation a satisfactory computation of the detonation velocity would not have been possible. On the other hand, they indicate, even in the equilibrium of very high concentrations of active particles, that the reaction velocity in detonation is very great.<sup>1</sup> By means of H<sub>2</sub> additions, the dissociation is greatly diminished; perhaps the result is that a diminished reaction velocity causes the discrepancy between observed and calculated detonation velocities at a higher H<sub>2</sub> content; this discrepancy has just been discussed. Whereas nitrogen and oxygen additions retard the detonation velocity (the influence of these two is somewhat different on account of their mass, which varies a little, and also because O<sub>2</sub>, as a reaction partner, dislocates the equilibriums of the dissociation), H<sub>2</sub> additions increase the detonation velocity and decrease the maximum temperature and pressure. This is one result of the hydrodynamic side of the phenomenon. From Eq. (10) for detonation velocity, it can be seen that a large specific volume (low density) is favorable for the detonation velocity. Lewis has concluded from this that dilution with an inert gas of low density (helium) must increase the detonation velocity. He has made very interesting experiments with He and A additions, the results of which

TABLE 31.—DETONATION VELOCITIES IN OXYGEN-HYDROGEN MIXTURES WITH ADDITION OF HELIUM AND ARGON (FROM LEWIS AND FRIEUF)  
Initial Temperature 291° Abs, Initial Pressure 1 Atm

| Mixture   | Detonation<br>pressure<br>$p_2$ , atm | Detonation<br>temperature<br>$T_2^\circ$ abs | Detonation velocity, m/sec |          |
|---|---------------------------------------|--|----------------------------|----------|
|   |                                       |  | Computed                   | Observed |
| (2H <sub>2</sub> + O <sub>2</sub> )                         | 18.05                                 | 3583   | 2806                       | 2819     |
| (2H <sub>2</sub> + O <sub>2</sub> ) + 1.5He                 | 17.60                                 | 3412   | 3200                       | 3010     |
| (2H <sub>2</sub> + O <sub>2</sub> ) + 3He                   | 17.11                                 | 3265   | 3432                       | 3130     |
| (2H <sub>2</sub> + O <sub>2</sub> ) + 5He                   | 16.32                                 | 3097   | 3613                       | 3160     |
| (2H <sub>2</sub> + O <sub>2</sub> ) + 2.82He }<br>+ 1.18A } | 16.68                                 | 3175   | 2620                       | 2390     |
| (2H <sub>2</sub> + O <sub>2</sub> ) + 1.5He }<br>+ 1.5A }   | 17.11                                 | 3265   | 2356                       | 2330     |
| (2H <sub>2</sub> + O <sub>2</sub> ) + 1.5A                  | 17.60                                 | 3412   | 2117                       | 1950     |
| (2H <sub>2</sub> + O <sub>2</sub> ) + 3A                    | 17.11                                 | 3265   | 1907                       | 1800     |
| (2H <sub>2</sub> + O <sub>2</sub> ) + 5A                    | 16.32                                 | 3097   | 1762                       | 1700     |

<sup>1</sup> Cf., however, p. 206.

together with the theoretical values of the detonation velocity are given in Table 31, shown on page 176.

The experiments confirm the expectations insofar as the He addition raises the detonation velocity whereas equal additions of argon lower it. Quantitatively, however—somewhat as is the case with hydrogen additions—the rise in velocity is less than is theoretically expected, and conversely an addition of argon lowers it more than expected. It is perhaps most reasonable to suppose that the reaction velocity is influenced. Probably the foreign gases play the part of one of the molecules of a triple collision in the recombination of active particles.

Before furnishing further numerical values, we wish to give a few details on the technique of measuring detonation velocities. The photographic method, which is applied most, is the same as that used in measuring flame velocities, except that it is necessary to work with considerably higher film speeds in detonation, and this gives rise to special problems. In the case of detonations that are weak in illumination,<sup>1</sup> it might be necessary to photograph with light from a foreign source. Thus shadows occur, and schlieren photographs result which have the advantage of permitting the photographing of ordinary shock waves. As we shall see later, it is interesting to photograph detonation waves with the aim in mind of detecting details. For this purpose, a high-speed film and good lenses are necessary if good results are expected.

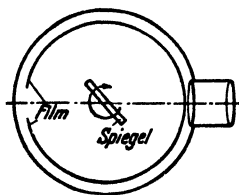
The speed of rotation of a film on a drum cannot be increased beyond a certain limit, or the film may loosen. Dixon, for example, had a drum of 1 m in circumference rotating at a speed of 100 m/sec, which is considerable if the film is to adhere. A substantial increase over this speed can be achieved only if films attached to the outside are dispensed with, since the centrifugal force makes too heavy a demand on them. A solution of the problem has been arrived at by two methods. The simplest of these was adopted by Payman, Shepherd, and Woodhead,<sup>2</sup> who fastened the film not on the outside but on the inside of a hollow drum that was closed and supported only at one end. By a suitable prism arrangement, the flame picture was projected on the inside of the drum. A speed of 400 rps was attained. Since the circumference of the drum is only 50 cm, the maximum film velocity is 200 m/sec. Still higher speeds can be attained if the film is attached to the inside of a stationary drum and the flame picture is allowed to rotate over the film. This is made possible by a rotating mirror attached to the axis of the

<sup>1</sup> At the time when Mallard and Le Chatelier made their measurements with the photographic method, the negatives were so insensitive that only especially luminous detonations ( $\text{CS}_2 + 3\text{O}_2$  and  $\text{CS}_2 + 6\text{NO}$ ) could be photographed.

<sup>2</sup> PAYMAN, W., W.C.F. SHEPHERD, and D.W. WOODHEAD, *Safety in Mines Research Board Paper* 99, London, 1937.

drum. Fraser<sup>1</sup> has built a camera of that kind in the Bone Institute (Fig. 118). The mirror (a double-faced steel mirror of high optical and mechanical precision) rotates with a maximum speed of 500 rps. Since the flame picture travels at double the speed of the mirror as the result of the laws of reflection, this is equivalent to a film velocity of 1000 rps, corresponding to a maximum picture velocity on the film of 1000 m/sec. The high degree of analysis possible with this camera has given us important information on the mechanism of detonation, particularly its beginning stages.

Schlieren photographs are used in Payman's<sup>2</sup> "wave velocity" camera, with which it is also possible to photograph shock waves. Laffitte<sup>3</sup> and his associates use shadow pictures, which are especially suited to the study of the detonation limits at which the luminous phenomena are weak. For the same purpose, Wendlandt<sup>4</sup> employed the



(Spiegel = mirror)

FIG. 118.

chronoelectric method by using a ballistic galvanometer as a measuring device. This method is relatively awkward, however, especially in determining detonation limits, as we shall see later. In experiments in which the detonation must cover a great distance (*e.g.*, in the chronoelectric method), lead tubes are generally used, sometimes rolled up on drums. The external form is of no importance. The same arrangement must be used if the detonation is to run for some distance in order that it is sure to be stationary. For photographing, a glass tube can be attached to the lead tube. Normally strong glass tubes do not always crack if a detonation runs through them. Sometimes it can be seen from the photographs that the glass has cracked after a reflected wave has gone through it one or more times; but it does not affect the photographs even if the glass shatters immediately, for the breaking is always a slow process compared with detonation, and thus a picture of the undisturbed detonation is obtained in spite of this. Often it is observed that a glass tube is able to withstand full detonation but bursts during its inception. We shall see that abnormally high pressures are noted especially in the initial stage.

<sup>1</sup> FRASER, R.P., *J. Roy. Photog. Soc.*, **74**, 388 (1934). A camera built on similar principles is also described by Payman, Shepherd, and Woodhead; see preceding footnote.

<sup>2</sup> PAYMAN, W., and H. ROBINSON, *Safety in Mines Research Board Paper* 29, 1927.

<sup>3</sup> LAFFITTE, P., and PATRIE, *Compt. rend.*, **191**, 1335 (1930). PATRIE, M., Thèse, Nancy, 1933. LAFFITTE, P., and M.J. BRETON, *Compt. rend.*, **199**, 146 (1934). BRETON, M.J., *Ann. office nat. des combust. liquides*, **11**, 487 (1936). See also "The Science of Petroleum," Vol. IV, 1938.

<sup>4</sup> WENDLANDT, R., *Z. physik. Chem.*, **110**, 637 (1924); **116**, 227 (1925).

A comprehensive view of the numerical values of detonation velocities is given for a series of detonating mixtures in Table 32 (taken from Laffitte, cited page 178).

A number of interesting conclusions can be drawn from the numerical values of observed detonation velocities. Dixon found the values in Table 33 for dry and moist CO.

TABLE 32.—DETONATION VELOCITIES AT ROOM TEMPERATURE AND ATMOSPHERIC PRESSURE (FROM LAFFITTE)

| Mixture  | $D$ , m/sec | Author              |
|--|-------------|---------------------|
| $2\text{H}_2 + \text{O}_2$ .....                                   | 2821        | Dixon               |
| $2\text{CO} + \text{O}_2$ .....                                    | 1264        | Dixon               |
| $\text{CS}_2 + 3\text{O}_2$ .....                                  | 1800        | Le Chatelier        |
| $\text{CH}_4 + 2\text{O}_2$ .....                                  | 2146        | Dixon               |
| $\text{CH}_4 + 1.5\text{O}_2 + 2.5\text{N}_2$ .....                | 1880        | Dixon               |
| $\text{C}_2\text{H}_6 + 3.5\text{O}_2$ .....                       | 2363        | Berthelot           |
| $\text{C}_2\text{H}_4 + 3\text{O}_2$ .....                         | 2209        | Dixon               |
| $\text{C}_2\text{H}_4 + 2\text{O}_2 + 8\text{N}_2$ .....           | 1731        | Dixon               |
| $\text{C}_2\text{H}_2 + 1.5\text{O}_2$ .....                       | 2716        | Dixon               |
| $\text{C}_2\text{H}_2 + 1.5\text{O}_2 + \text{N}_2$ .....          | 2114        | Dixon               |
| $\text{C}_3\text{H}_8 + 3\text{O}_2$ .....                         | 2600        | Laffitte and Breton |
| $\text{C}_3\text{H}_8 + 6\text{O}_2$ .....                         | 2280        | Laffitte and Breton |
| $i\text{-C}_4\text{H}_{10} + 4\text{O}_2$ .....                    | 2613        | Laffitte and Breton |
| $i\text{-C}_4\text{H}_{10} + 8\text{O}_2$ .....                    | 2270        | Laffitte and Breton |
| $\text{C}_5\text{H}_{12} + 8\text{O}_2$ .....                      | 2371        | Dixon               |
| $\text{C}_5\text{H}_{12} + 8\text{O}_2 + 24\text{N}_2$ .....       | 1680        | Dixon               |
| $\text{C}_6\text{H}_6 + 7.5\text{O}_2$ .....                       | 2206        | Dixon               |
| $\text{C}_6\text{H}_6 + 22.5\text{O}_2$ .....                      | 1658        | Dixon               |
| $\text{C}_2\text{H}_5\text{OH} + 3\text{O}_2$ .....                | 2356        | Dixon               |
| $\text{C}_2\text{H}_5\text{OH} + 3\text{O}_2 + 12\text{N}_2$ ..... | 1690        | Dixon               |

The great increase of detonation velocity by small additions of vapor can be explained only by the increase in reaction velocity. Small percentages of  $\text{H}_2\text{O}$  cannot influence the density and temperature of the detonation wave to such an extent as to bring about an increase of the velocity by about one-third. At higher  $\text{H}_2\text{O}$  partial pressures, the rarefaction effect makes itself felt. The influence of the reaction velocity is again to be understood as too small in a dry mixture to cause a detonation (under Dixon's experimental conditions) with the velocity that is proper to the reaction  $2\text{CO} + \text{O}_2 = 2\text{CO}_2$ . Only small additions of vapor cause a sufficiently rapid appearance of equilibrium in accord with other findings in this reaction (*cf.* Chaps. III and IX).

Dixon has tested this influence of the reaction velocities experimentally by photographing the combustion. Through a window on a rotating drum, he selected a location on the tube through which the

TABLE 33.—DETONATION VELOCITIES OF DRY AND MOIST MIXTURES OF  $2\text{CO} + \text{O}_2$ ,  
(FROM DIXON)

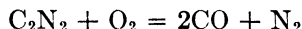
| Condition of the gas  | % water vapor | <i>D</i> , m/sec |
|---|---------------|------------------|
| Dried with $\text{H}_2\text{SO}_4 + \text{P}_2\text{O}_5$ ..... | —             | 1264             |
| Dried with $\text{H}_2\text{SO}_4$ .....                        | —             | 1305             |
| Saturated with water vapor at $10^\circ\text{C}$ .....          | 1.2           | 1676             |
| Saturated with water vapor at $20^\circ\text{C}$ .....          | 2.3           | 1703             |
| Saturated with water vapor at $28^\circ\text{C}$ .....          | 3.7           | 1713             |
| Saturated with water vapor at $35^\circ\text{C}$ .....          | 5.6           | 1738             |
| Saturated with water vapor at $45^\circ\text{C}$ .....          | 9.5           | 1693             |
| Saturated with water vapor at $55^\circ\text{C}$ .....          | 15.6          | 1666             |
| Saturated with water vapor at $65^\circ\text{C}$ .....          | 24.9          | 1526             |
| Saturated with water vapor at $75^\circ\text{C}$ .....          | 38.4          | 1266             |

detonation passed. The length of the picture thus obtained gives a certain measure for the time needed for combustion. It was shown that, in a moist mixture of  $2\text{CO} + \text{O}_2$ , the combustion was extinguished in less than half the time required for its course in a dry mixture. It will be necessary to be cautious with quantitative conclusions from this finding, since vapor also influences the radiation properties of carbon monoxide flames.

More striking and more definite still are the phenomena in cyanogen detonation, according to Dixon.<sup>1</sup> The detonation velocities of various cyanogen-oxygen mixtures are

|                                     |  |   |
|-------------------------------------|--|---|
| $\text{C}_2\text{N}_2 + \text{O}_2$ | $\text{C}_2\text{N}_2 + 2\text{O}_2$             | $\text{C}_2\text{N}_2 + 3\text{O}_2$              |
| 2728 m/sec                          | 2321 m/sec                                       | 2110 m/sec  |
|                                     | $\text{C}_2\text{N}_2 + \text{O}_2 + \text{N}_2$ | $\text{C}_2\text{N}_2 + \text{O}_2 + 2\text{N}_2$ |
|                                     | 2398 m/sec                                       | 2166 m/sec  |

The mixture that burns according to the formula



has the highest detonation velocity. Dixon therefore concluded that conversion in the detonation zone goes only to CO and that, in case of oxygen excess, the rest of the combustion takes place behind the detonation zone. This is proved by the experiments cited above, in which nitrogen instead of excess oxygen is added. If nitrogen is used instead of oxygen, the detonation velocity not only is not decreased but is rather somewhat increased on account of the smaller density (*cf.* pages 176–177). Here too Dixon furnishes direct experimental proof, by means of photographs, of the fact that the reaction lasts longer with excess oxygen. The reaction  $\text{C}_2\text{N}_2 + 2\text{O}_2$  requires many times the period to run its

<sup>1</sup> DIXON, H.B., *Trans. Chem. Soc.*, 1896, p. 759.

course that suffices for the reaction  $C_2N_2 + O_2$  (cf. the reproductions in Bone and Townend, page 156).

The situation in the detonation of hydrocarbons is not quite so distinct as in the foregoing cases. The results show once more that the greatest detonation velocity is reached in mixtures whose oxygen content does not suffice for combustion into  $CO_2 + H_2O$ , as the following examples from Bone show:

|                |                           |                           |           |
|----------------|---------------------------|---------------------------|-----------|
| $CH_4 + O_2$   | $CH_4 + \frac{3}{2}O_2$   | $CH_4 + 2O_2$             | Methane   |
| 2528 m/sec     | 2470 m/sec                | 2322 m/sec                |           |
| $C_2H_4 + O_2$ | $C_2H_4 + 2O_2$           | $C_2H_4 + 3O_2$           | Ethylene  |
| 2507 m/sec     | 2581 m/sec                | 2368 m/sec                |           |
| $C_2H_2 + O_2$ | $C_2H_2 + \frac{3}{2}O_2$ | $C_2H_2 + \frac{5}{2}O_2$ | Acetylene |
| 2961 m/sec     | 2716 m/sec                | 2391 m/sec                |           |

If a part of the oxygen is replaced with nitrogen in the mixture, which suffices for complete combustion into carbonic acid and water, a slight increase in the detonation velocity appears, for example,

|                 |                       |
|-----------------|-----------------------|
| $C_2H_4 + 3O_2$ | $C_2H_4 + 2O_2 + N_2$ |
| 2368 m/sec      | 2413 m/sec            |

The conclusion drawn by Bone that not all oxygen in the wave front is used in detonation with sufficient oxygen is not necessarily wrong, but it does not appear to be conclusive here; for, if (disregarding dissociation for the time being) the first mixture burns into  $2CO_2 + 2H_2O$ , it has an essentially greater density than the second with the terminal composition  $2CO + 2H_2O + N_2$ . The considerable difference in density could cause the greater detonation velocity in the second case even at a somewhat lower combustion temperature. Since obviously in such cases no true equilibriums are reached, but rather conditions in which the one or the other conversion is to be regarded as more inhibited, a theoretical treatment is uncertain. For example, Dixon found the following composition of the cold gases in the detonation of  $C_2H_6 + O_2$  with a velocity of 2180 m/sec:

|                 |                |                            |
|-----------------|----------------|----------------------------|
| $CO_2 = 0.75\%$ | $CO = 38.55\%$ | $C_2H_2 + C_2H_4 = 1.10\%$ |
| $CH_4 = 8.15\%$ | and            | $H_2 = 51.1\%$             |

in addition to condensed water and solid carbon. Apparently similar reactions occur in the detonation of hydrocarbons as in the slow oxidation and the purely thermal disintegration as well as in ordinary explosion (Bone, cited page 156); cf. also Chap. XI.

**4. Detonation Limits.**—The location of detonation limits was first systematically investigated by Wendlandt (cited page 178). Although detonation can be induced relatively easily in the more explosive mixtures, sometimes by means of a powerful spark or, in ordinary ignition,

by means of a moderately long flame, it becomes more and more difficult to produce the detonation wave in less explosive mixtures, especially near the detonation limits. It is then necessary to employ an initial ignition, as is done with solid explosives. For this purpose, either solid initial explosives are used (lead azide, fulminate of mercury) or the mixture in a lengthy tube is allowed to communicate with a second tube by means of a pet cock of the same bore if possible as the diameter of the detonation tube. In the second tube is a readily detonating mixture, like an oxygen-hydrogen mixture, which is ignited. If the detonation in a mixture difficult to detonate is brought about by means of the rapid detonation wave of a mixture easy to detonate, an excessive velocity is frequently obtained at the beginning because of the greater impulse of the initial explosive, which only gradually declines to that of the

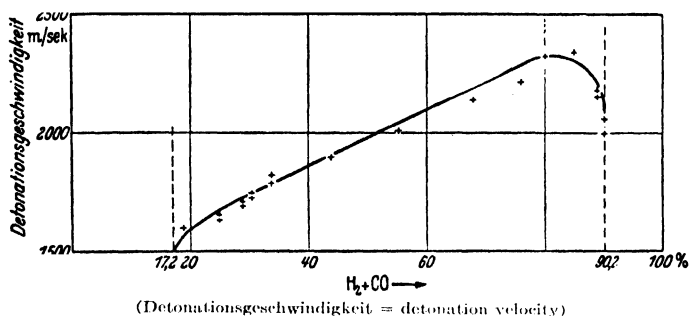


Fig. 119.—Detonation limits of  $H_2 + CO$  in  $O_2$ . (From Breton, p. 180.)

stationary detonation. A detonation wave can also, by means of this added impulse, be produced in mixtures in themselves not capable of detonation. The wave is not stable, however, but declines and is finally extinguished. It is therefore easy to be deceived if the detonation is observed only in a tube of 1 to 2 m in length directly connected to the initial tube. It is necessary instead to make sure in a longer tube whether the detonation still exists and whether it is proceeding with stationary, constant velocity (sometimes many meters of lead tubing are required for adequate observation). Only if this is the case does real detonation exist and can the detonation limits be safely determined. Wendlandt has applied all these precautions in his investigation. The method of the later experiments by Laffitte and collaborators (who investigated a great number of materials and confirmed Wendlandt's results in the case of  $CO$  and  $H_2$ ) has already been mentioned (page 178). In Figs. 119 and 120, two typical curves are given that were obtained by Breton<sup>1</sup> in the laboratory of Laffitte for the detonation velocity in determining the detonation limits. In the neighborhood of both limits, the detonation

<sup>1</sup> BRETON, M.J., *Ann. office nat. des combust. liquides*, **11**, 487 (1936).

velocity drops sharply. Numerical values for detonation limits (chiefly from Laffitte and his associates) are given in Table 34.

The limits, as can be expected and as a comparison with the values given in Chap. III, page 132, shows, are narrower than for ordinary explosion. Just as the values of the lower limit, which is determined by lack of fuel, do not vary much for air and oxygen with normal ignition, so this is also true of detonation, even though with somewhat greater variations.

Several peculiarities must still be emphasized. Breton has investigated the influence of hydrogen on the lower detonation limit of  $2\text{CO} + \text{O}_2$ . Substitution of 2 per cent of the CO by  $\text{H}_2$  decreases the lower detonation limit from 38 to 28.4 per cent.<sup>1</sup> Once more this is a

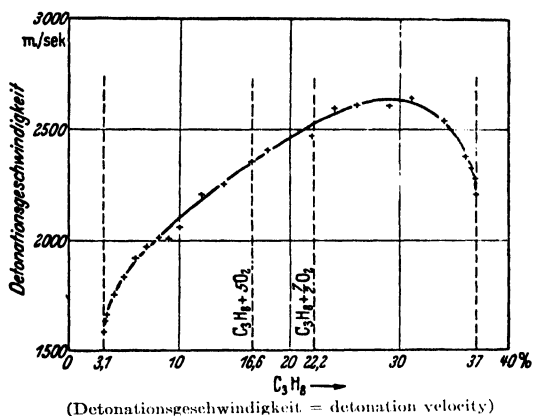


Fig. 120.—Detonation limits of propane in oxygen. (From Breton.)

confirmation of the reaction-accelerating effect of hydrogen or  $\text{H}_2\text{O}$  on carbon monoxide combustion observed in many phenomena. A peculiarity that must likewise be caused by the sluggishness of CO was observed by Le Chatelier. The shock wave produced by 0.75 grams of fulminate of mercury does not ignite a mixture of  $2\text{CO} + \text{O}_2$  because the wave is too fast and the CO combustion cannot follow. On the other hand, it is possible to cause detonation of carbon monoxide regularly with the detonation of only 0.05 grams of fulminate of mercury.

Breton has made very special observations with  $\text{NH}_3\text{-O}_2$  mixtures. Here, although not in all experiments, a rise in the detonation velocity is observed near both limits. At the upper limit, this is best explained by the liberation of  $\text{H}_2$  and the consequent lowering of the density. What takes place at the other limit is not as yet clear.

<sup>1</sup> For further information on the  $\text{H}_2$  influence, see Breton, cited p. 182 and Laffitte, cited p. 178.

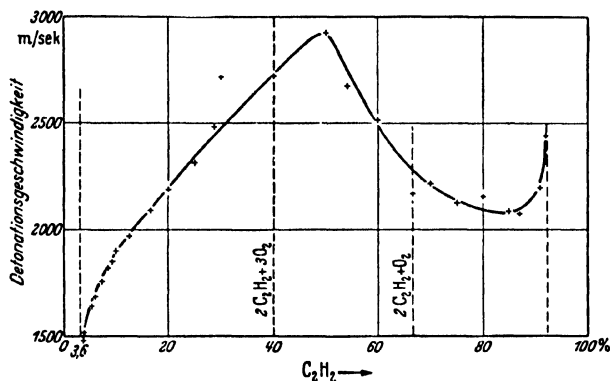


TABLE 34.—DETONATION LIMITS (FROM BRETON<sup>1</sup> AND LAFFITTE<sup>2</sup>)

| Mixture   | % fuel in air or oxygen |             |
|---|-------------------------|-------------|
|   | Lower limit             | Upper limit |
| H <sub>2</sub> -O <sub>2</sub> .....  | 15                      | 90          |
| H <sub>2</sub> -Air.....  | 18.3                    | 58.9        |
| CO-O <sub>2</sub> , moist.....  | 38                      | 90          |
| CO-O <sub>2</sub> , dried with H <sub>2</sub> SO <sub>4</sub> and P <sub>2</sub> O <sub>5</sub> ..... | —                       | 83          |
| (CO + H <sub>2</sub> )-O <sub>2</sub> .....   | 17.2                    | 91          |
| (CO + H <sub>2</sub> )-air.....   | 19                      | 58.7        |
| NH <sub>3</sub> -O <sub>2</sub> .....   | 25.4                    | 75.4        |
| C <sub>3</sub> H <sub>8</sub> -O <sub>2</sub> .....   | 3.2                     | 37          |
| iso-C <sub>4</sub> H <sub>10</sub> -O <sub>2</sub> .....  | 2.8                     | 31.1        |
| C <sub>2</sub> H <sub>2</sub> -O <sub>2</sub> .....   | 3.5-3.6                 | 92-93       |
| C <sub>2</sub> H <sub>2</sub> -air.....   | 4.2                     | 50          |
| C <sub>4</sub> H <sub>10</sub> O(ether)-O <sub>2</sub> .....  | 2.6-2.7                 | >40         |
| C <sub>4</sub> H <sub>10</sub> O-air.....   | 2.8                     | 4.5         |

<sup>1</sup> BRETON, M. J., *Ann. office nat. combust. liquides*, **11**, 487 (1936).<sup>2</sup> LAFFITTE, P., "The Science of Petroleum," Vol. IV, p. 2995, 1938.

Noteworthy, too, are Breton's results in the case of acetylene (Fig. 121). Acetylene-air mixtures show results analogous to those obtained with oxygen, only less definite. At the lower limit, the mixture is normal. In the neighborhood of 50 per cent (in a mixture with air at considerably



(Detonationsgeschwindigkeit = detonation velocity)

FIG. 121.—Detonation limits of acetylene in oxygen. (From Breton.)

smaller concentrations), the detonation velocity passes through a maximum, so that one would expect the detonation limit just beyond this value. This is, however, not at all the case. Instead, the detonation velocity drops rather rapidly, passes through a minimum, and then rises once more to the upper detonation limit at 92 to 93 per cent. According to Breton and Laffitte, two distinct processes are at work

here: In smaller acetylene concentrations, we are dealing with detonation as a result of combustion; whereas, at higher concentrations, the main reaction is perhaps the disintegration of the acetylene introduced by combustion.

**5. Influence of External Factors on Induction and Propagation of Detonation.**—In the theory of detonation velocity, use has been made of the fact that detonation progresses in a tube of constant cross section. If the detonation tube is suddenly widened, the impulse of the wave is transferred to a much larger mass of gas, and the velocity of the wave is correspondingly inhibited so that the detonation can fail to take place. Instead, a flame sometimes progresses. If the second tube is long enough, a second detonation wave can form at some distance. Such phenomena were first observed by Campbell<sup>1</sup> in 1922, and Laffitte,<sup>2</sup> among others, carried out further investigations. He determined the distances that would have to be traversed by the flame after it entered the wider tube until detonation would again occur. These results are given in Table 35 for the mixture  $\text{CS}_2 + 3\text{O}_2$ , the detonation having progressed in a tube of 7 mm diameter with a velocity of 1800 m/sec. It

TABLE 35.—RECURRENCE OF THE DETONATION AFTER LEAVING A TUBE 7 MM IN DIAMETER AND ENTERING A SECOND TUBE (FROM LAFFITTE) FOR  $\text{CS}_2 + 3\text{O}_2$

| Diameter of the<br>Second Tube, Mm | Distance in the Second Tube at Which<br>Detonation Again Appeared, Cm |
|------------------------------------|---|
| 13                                 | 8   |
| 16                                 | 9   |
| 24                                 | 15  |
| 33                                 | 50  |
| 44                                 | 100   |

can be seen that the wider the tube, the more difficult it is for detonation to form again. The same effect is present in the spontaneous detonation arising from a flame. Laffitte gives the following data for the same mixtures according to Table 36. Remarkably enough, a raising of the initial temperature also has a retarding effect on the origin of detonation.

TABLE 36

| Diameter of the<br>Tube, Mm | Distance from the Spark at Which<br>Detonation Appears, Cm |
|-----------------------------|--|
| 6.5-7                       | 48   |
| 16                          | 52   |
| 24                          | 58   |
| 34                          | 84   |
| 43                          | 105  |
| 54                          | 131  |

<sup>1</sup> CAMPBELL, J., *J. Chem. Soc.*, **121**, 2483 (1922).

<sup>2</sup> LAFFITTE, P., *Compt. rend.*, **177**, 178 (1923); **179**, 1394 (1924). *Ann. phys.*, (X), **4**, 623 (1925).

Laffitte<sup>1</sup> has also conducted experiments on this phenomenon, and we record the results in Table 37.

TABLE 37.—FLAME PATHS THAT MUST BE TRAVERSED TILL THE APPEARANCE OF DETONATION (FROM LAFFITTE)  
For Various Temperatures

| $2H_2 + O_2$               |   | $CH_4 + 2O_2$              |   |
|----------------------------|---|----------------------------|---|
| Initial temperature,<br>°C | Distance,<br>cm                         | Initial temperature,<br>°C | Distance,<br>cm                         |
| 15                         | 60                                      | 15                         | 55                                      |
| 120-130                    | 73                                      | 160-180                    | 74                                      |
| 160-180                    | 78                                      | 290-310                    | 90                                      |
| 300-320                    | { No detonation in<br>the tube 1 m long | 340-360                    | { No detonation in<br>the tube 1 m long |
| 340-360                    |   |                            |   |

In judging these experiments, it should be remembered that a corresponding decrease in concentration is connected with a rise in temperature at constant pressure.

According to experiments by Dixon,<sup>2</sup> the detonation velocity also decreases somewhat with the temperature, though not very much (Table 38).

TABLE 38

| Temperature,<br>°C | $D$ , m/sec  |                 |
|--------------------|--------------|-----------------|
|                    | $2H_2 + O_2$ | $C_2H_4 + 2O_2$ |
| 10                 | 2821         | 2581            |
| 100                | 2790         | 2538            |

Conversely, a rise in pressure has a favorable effect on the induction of detonation and (to a smaller degree) on the detonation velocity. For the induction of detonation, we shall cite several experiments by Laffitte and Dumanois<sup>3</sup> as well as by Egerton and Gates,<sup>4</sup> which show clearly that the distance to be traversed until detonation takes place becomes shorter the higher the initial pressure. At this point, the observation by Bone, Newitt, and Townend<sup>5</sup> should be mentioned that, in

<sup>1</sup> LAFFITTE, P., *Compt. rend.*, **186**, 951 (1928).

<sup>2</sup> DIXON, H.B., *Phil. Trans. Roy. Soc. London*, A, **184**, 97 (1893); **200**, 315 (1903).

<sup>3</sup> LAFFITTE, P., and P. DUMANOIS, *Compt. rend.*, **183**, 284 (1926).

<sup>4</sup> EGERTON, A., and S.F. GATES, *Proc. Roy. Soc. London* A, **114**, 152 (1927); **116**, 516 (1927).

<sup>5</sup> BONE, W.A., D.M. NEWITT, and D.T.A. TOWNEND, *Proc. Roy. Soc. London*, A, **139**, 57 (1933).

high-pressure explosions of  $2\text{H}_2 + \text{O}_2 + 3.76\text{N}_2$  at 500 atm initial pressure, a completely steady course was noted, whereas at 750 atm initial-pressure violent detonation appeared at once and caused considerable damage to the apparatus. The influence of the pressure on the velocity of oxygen-hydrogen detonation is shown by the following table for  $2\text{H}_2 + \text{O}_2$ , according to experiments by Dixon:

|                  |      |      |      |      |      |      |
|------------------|------|------|------|------|------|------|
| $p$ , mm Hg..... | 200  | 300  | 500  | 760  | 1100 | 1500 |
| $D$ , m/sec..... | 2627 | 2705 | 2775 | 2821 | 2856 | 2872 |

Thus there is a clear even though small increase of the detonation velocity with the increase in pressure. Theoretically there is no direct pressure influence as long as one is in the range of validity of the ideal law of gases; however, there is an indirect influence in reactions that take place with a change of mol-number where the pressure displaces the equilibrium. Especially the water and  $\text{H}_2$  dissociations are retarded by pressure (*cf.* Chap. VII). This influence might suffice completely to explain the increase in detonation velocity through pressure found by Dixon.

TABLE 39.—THE DISTANCE TO BE TRAVERSED BY THE FLAME TILL THE APPEARANCE OF DETONATION  
For Various Initial Pressures

| Laffitte and Dumanois (25 mm tube)<br>$2\text{H}_2 + \text{O}_2$ |                 | Egerton and Gates (15.9 mm tube)<br>$\text{C}_2\text{H}_2 + 2.5\text{O}_2 + 4\text{N}_2$ |             |
|--|-----------------|--|-------------|
| Initial pressure,<br>atm   | Distance,<br>cm | Initial pressure,<br>atm   | Path,<br>cm |
| 1  | 70              | 1  | 52          |
| 2  | 60              | 2  | 30          |
| 3  | 52              |  |             |
| 4  | 44              | 3.7  | 22          |
| 5  | 35              |  |             |
| 6  | 30              | 4.1  | 18          |
| 6.5  | 27              |  |             |

Correspondingly, a small extension of the detonation limits through pressure is to be expected, and this was found to be the case by Breton (*cited* page 182). The detonation limits for  $\text{H}_2\text{-O}_2$ , which amount to 15 and 90 per cent at normal pressure, are extended by 8 atm of initial pressure to  $\sim 14$  and 91 per cent. In other cases, the influence is similar to this.

Just as a detonation wave is extinguished when entering a wider tube from a narrower one, so a spreading of the detonation wave in open

space is not possible. Attempts to detonate a mixture enclosed in a large glass sphere by ignition at the center will fail, as could be expected, even if a detonation wave that has been coursing through a tube that terminates in the center of the sphere is used for ignition. If, however, detonation is induced not by simple ignition or by the detonation wave of a gaseous mixture but rather by means of a sufficiently powerful explosive, *e.g.*, mercury fulminate, then detonation waves can be observed also in spheres. Laffitte<sup>1</sup> could thus observe the detonation of  $\text{CS}_2 + 3\text{O}_2$  and  $2\text{H}_2 + \text{O}_2$  in a large glass sphere. It is to be assumed that this was not a completely independent, stationary detonation wave but that the auxiliary effect of the shock wave of the explosive is an important factor.

Payman and Shepherd<sup>2</sup> have shown that, by means of very violent initial ignition, it is possible to obtain a detonation-like combustion with velocities in the order of magnitude of those of detonation in methane-air mixtures which are in themselves not capable of detonation. This process they call quasidetonation. Velocities of 1900 m/sec were obtained, but they are not stationary as in a real detonation.

Weissweiler<sup>3</sup> made remarkable observations in determining the explosion limits ("ignition limits") of chlorine and hydrogen mixtures in bombs. He observed extraordinarily steep, detonation-like pressure increases in the proximity of the lower ignition limit (*e.g.*, with 7 to 9 per cent  $\text{H}_2$  in chlorine). Similar observations were made in  $\text{H}_2\text{-O}_2$  (or air) mixtures. An explanation for the observations is lacking. It is probably not a matter of a regular detonation wave, if only for purely geometrical reasons; but it is a matter of an extraordinarily rapid reaction of a part (or of the whole) of the mixture, quite as in the case of knocking in an engine (*cf.* Chap. XII).

**6. Detonation Pressures.**—In the mechanical effects of a detonation (or shock) wave, the steepness of the wave front and the sudden and discontinuous pressure effect caused by it play a special role. The detonation pressures are about of the order of magnitude of 20 atm and in the most extreme case (atmospheric pressure always assumed as the initial condition) perhaps double that.<sup>4</sup> As already discussed (page 168), it is necessary to differentiate between the hydrostatic pressure in the wave and the total impulse, in which the impulse of the burned gases striving to the front is contained in addition to the stationary pressure.

<sup>1</sup> LAFFITTE, P., *Compt. rend.*, **177**, 178 (1923); **179**, 1394 (1924).

<sup>2</sup> PAYMAN, W., and W.C.F. SHEPHERD, *Proc. Roy. Soc. London, A*, **158**, 348 (1937). Attention is called to these works because they also have a series of interesting detonation and schlieren photographs.

<sup>3</sup> WEISSWEILER, A., *Z. Elektrochem.*, **42**, 499 (1936).

<sup>4</sup> From the estimates of Langweiler (cited p. 172), it follows that the detonation pressure must always remain smaller than twice the pressure that would appear in an explosion in a closed container.

In a manometer affixed to the side of the tube, the hydrostatic pressure would be measured, insofar as it would be possible to measure pressures at all in the extremely short time available. With the aid of piezo quartz, such measurements would perhaps not be entirely excluded. The method commonly used formerly of determining the detonation pressure from the breaking of glass tubes tested as to their tensile strength by static pressure seems to be inadmissible as a matter of principle, since conditions in the pressure effect of the wave front, which itself changes erratically and in addition lasts only a short time, are not comparable with those at static pressure.

TABLE 40.—DETONATION PRESSURES (FROM CAMPBELL, LITTLER, AND WHITWORTH)

| Mixture   | <i>p</i> observed,<br>atm | <i>p</i> observed, atm |  |
|---|---------------------------|------------------------|--|
|   |                           | Jouguet                | Campbell,<br>Littler, and<br>Whitworth |
| 2H <sub>2</sub> + O <sub>2</sub> .....                  | 20.4                      | 17.5                   | —                                      |
| CH <sub>4</sub> + O <sub>2</sub> .....                  | 34.0                      | —                      | 36.3                                   |
| CH <sub>4</sub> + 4O <sub>2</sub> .....                 | 26.0                      | —                      | 25.9                                   |
| C <sub>2</sub> H <sub>4</sub> + 2O <sub>2</sub> .....   | 41.5                      | —                      | 41.0                                   |
| C <sub>2</sub> H <sub>4</sub> + 3O <sub>2</sub> .....   | 34.0                      | —                      | 31.6                                   |
| C <sub>2</sub> H <sub>2</sub> + O <sub>2</sub> .....    | 41.5                      | 54.5                   | —                                      |
| C <sub>2</sub> H <sub>2</sub> + 2.5O <sub>2</sub> ..... | 34.0                      | —                      | 30.0                                   |
| C <sub>2</sub> H <sub>2</sub> + 7.5O <sub>2</sub> ..... | 26.0                      | —                      | 25.8                                   |

The total impulse would affect a plate placed perpendicularly in the path of the detonation wave. The corresponding method of determining the pressure from the piercing of metal strips that have been statically calibrated and placed in the path of the detonation wave is perhaps subject to fewer objections than the breaking of a glass tube, for in the former method at least the entire surface is equally affected. The effect of the pressure is very brief, however, and it is therefore not certain whether the static calibration is entirely dependable for this purpose. At any rate, the detonation pressures measured by Campbell, Littler, and Whitworth<sup>1</sup> according to this method are in good agreement with the computed theoretical values.

It is significant that, at the moment of origin of the detonation wave, the pressures are essentially higher and can be up to twice as high as in the stationary wave itself. This is in agreement with other observations on the origin of the detonation wave (*cf.* pages 196*ff.*). Numerical values for the measured detonation pressures are given in Table 40,

<sup>1</sup> CAMPBELL, F.C., W.B. LITTLER, and C. WHITWORTH, *Proc. Roy. Soc. London*, **137**, 380 (1932).

according to Laffitte. In comparing the measured with the computed pressures, it should be noted that the values computed by Jouguet are not very accurate, because of the older data on specific heats, etc. In computing the detonation of hydrocarbons, it would be necessary to know what terminal condition is reached in the detonation zone. Considering these facts, it is permissible to regard the agreement between measured and computed detonation pressures as satisfactory.

**7. Influence of Additions on the Origin of Detonations.**—Because of its nature, the detonation process is in general considerably independent of small impurities in the experimental gases. When equilibrium is attained in the detonation wave, a marked influence of its velocity is only then possible if this equilibrium is displaced; but for this purpose impurities in small concentrations are inadequate. The situation is different if no equilibrium is reached in the wave front, as is sometimes the case in CO-O<sub>2</sub> detonations. In the latter case, it is possible as a result to influence the appearance of equilibrium and hence the detonation velocity considerably by small amounts of reaction-accelerating additions like vapor (*cf.* page 180). Carbon monoxide combustion, however, is an exception in this regard.

The situation is still different if the complete detonation is not considered but rather the process of originating a detonation from a combustion that is at first regular. We have noted above (pages 185–186) the influence of external factors like tube diameter and temperature on this “predetonation period” (expressed perhaps by the length of the path to be covered by the flame). Systematic investigations on the influences affecting the origin of the detonation wave have been made by Sokolik and Shtsholkin.<sup>1</sup> Dixon<sup>2</sup> and Laffitte and Dumanois<sup>3</sup> have determined (as was to be expected) that the detonation velocity is not influenced by the addition of lead tetraethyl. Further, Egerton and Gates<sup>4</sup> found that, in the case of pentane mixtures [C<sub>5</sub>H<sub>12</sub> + 8O<sub>2</sub> + 2N<sub>2</sub> and C<sub>5</sub>H<sub>12</sub> + 8O<sub>2</sub> + 6N<sub>2</sub>(15N<sub>2</sub>)] with initial pressures of up to 5.8 atm, the addition of lead tetraethyl in concentrations up to over one part per thousand did not delay the appearance of detonation.

Sokolik and Shtsholkin observed that, under certain circumstances at low pressures (about 50 to 500 mm Hg), the dependence of the “predetonation path” (*i.e.*, the distance the flame must traverse before it can change into detonation) on the pressure can be quite remarkable and that, under these circumstances, the predetonation path can furthermore

<sup>1</sup> SOKOLIK, A., and K. SHTSHOLKIN, *Sovet. Phys.*, **4**, 195 (1933). SHTSHOLKIN, K., and A. SOKOLIK, *Acta Physicochim. URSS*, **7**, 581, 589 (1937).

<sup>2</sup> DIXON, H.B., *Trans. Faraday Soc.*, **22**, 372 (1926).

<sup>3</sup> LAFFITTE, P., and P. DUMANOIS, *Compt. rend.*, **186**, 146 (1928).

<sup>4</sup> EGERTON, A., and S.F. GATES, *Proc. Roy. Soc. London, A*, **114**, 149 (1928).

be lengthened by the addition of lead tetraethyl. "Pentane" (namely, a petrol-ether fraction boiling from 38° to 40°C) in mixtures with oxygen as well as oxygen plus nitrogen was used for the experiments. The results are given in Fig. 122. In the case of pentane-oxygen (1), a smooth curve is obtained agreeing with other observations. However, as soon as some nitrogen is added (2), the curve takes on a more steplike form, which becomes more marked as the nitrogen is increased (3). A similar curve is noted in the case of oxygen-hydrogen mixtures (without nitrogen) (4). The paths of the curves show a certain similarity with relations found by

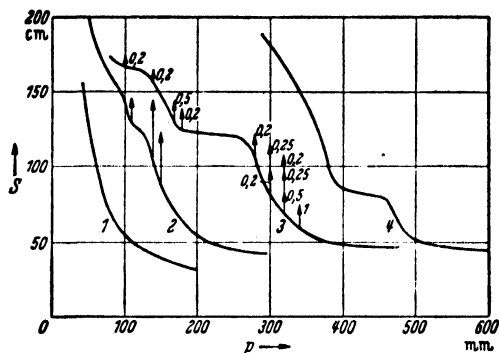


FIG. 122.—Dependence of the predetonation path on the pressure for  $C_5H_{12} + 8O_2$ (1),  $C_5H_{12} + 8O_2 + 2N_2$ (2),  $C_5H_{12} + 8O_2 + 3N_2$ (3),  $2H_2 + O_2$ (4). Arrows indicate change of the predetonation path by the addition of the per cent  $Pb(eth)_4$  noted. (From Shtsholkin and Sokolik.<sup>1</sup>)

Townend and his collaborators<sup>2</sup> between auto-ignition temperatures and pressures for hydrocarbons.

In Fig. 123, the same is given again for the mixture  $C_5H_{12} + 8O_2 + 2N_2$ ; in addition, the curve shown by a dotted line which is obtained if 1.2 per cent  $Pb(eth)_4$  is added to this mixture, *i.e.*, a great amount compared with that used in running engines. As can be seen, predetonation paths in some pressure ranges can be considerably increased by this addition. The most reasonable explanation for this phenomenon is that a certain minimum reaction velocity is attained in the fresh gas compressed by the accelerated flame until detonation takes place. If this velocity is inhibited by  $Pb(eth)_4$ , the appearance of detonation is retarded.

Shtsholkin and Sokolik have also made experiments in which pentane-oxygen mixtures were heated to temperatures between 300° and 400°C

<sup>1</sup> SOKOLIK, A., and K. SHTSHOLKIN, *Sovjet. Phys.*, **4**, 195 (1933). SHTSHOLKIN, K., and A. SOKOLIK, *Acta Physicochim.*, URSS, **7**, 581, 589 (1937).

<sup>2</sup> TOWNEND, D.T.A., and M.R. MANDLEKAR, *Proc. Roy. Soc. London, A*, **141**, 484 (1933) and later works; *cf.* Chap. XI; "The Science of Petroleum," Vol. IV, 1938, as well as *Chem. Rev.*, **21**, 259 (1937).



under pressures of 300 mm, *i.e.*, in a range in which cold flames appear with induction periods of the order of magnitude 1 to several seconds from the introduction of the gas on. The experiments were carried out in such a manner that, at various times from the time of the introduction of the gas into the same detonation tube, the mixture was ignited by a spark. It is demonstrated that the predetonation path (see above) is considerably shortened if the ignition takes place with the appearance of the cold flame or shortly thereafter. If, however, ignition takes place some time after the appearance of the cold flame, the length of the predetonation path is again extended, and sometimes no ignition takes place

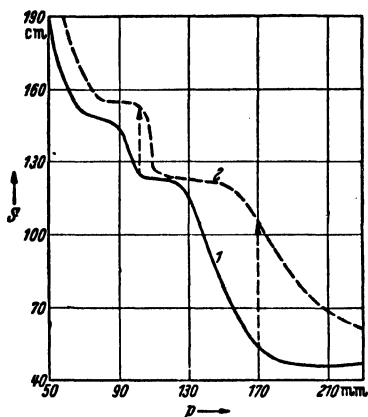


FIG. 123.—Dependence of the predetonation path on the pressure for  $C_4H_{12} + 8O_2 + 2N_2(l)$  as well as for the same mixture 1.2 per cent  $Pb(eth)_4$ . (From Shtsholkin and Sokolik.)

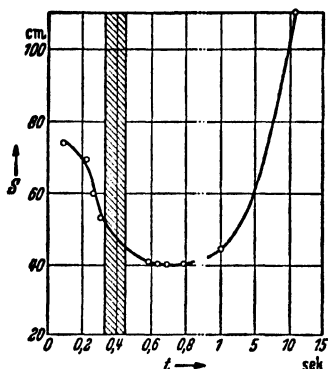


FIG. 124.—Dependence of the predetonation path on the ignition instant, for pentane-air, 10 per cent superrich. (From Shtsholkin and Sokolik.)

at all. The results of a number of experiments, all of which were made at  $335^\circ C$  and 320 mm pressure, are given in Fig. 124. The predetonation path is plotted as a function of the time of ignition (from the introduction of the mixture). The shaded section in Fig. 124 corresponds to the interval of time (0.4 sec) in which the cold flames appear. Naturally, similarities between these observations and the knocking process in engines suggest themselves (*cf.* Chap. XII).

**8. Relation between Percussion Wave and Detonation: "Spin" of Detonations.**—The most remarkable phenomenon connected with detonation is the so-called "spin," which has been discovered only recently.<sup>1</sup> It was first observed by Campbell and Woodhead. By "spin" the following is meant: In the case of some detonating mixtures,

<sup>1</sup> CAMPBELL, C., and D.W. WOODHEAD, *J. Chem. Soc.*, 1926, p. 3010; 1927, p. 1572. CAMPBELL, C., and A. FINCH, *J. Chem. Soc.*, 1928, p. 2094.

for example,  $2\text{CO} + \text{O}_2$ , photographs made with great speed reveal an undulating wave front and a striped effect of the flame picture closely connected with this waviness (Fig. 125 taken from Bone and Fraser).<sup>1</sup> The most obvious explanation is that it is a matter of a luminous phenomenon accompanying the gas, which is rotated around the longitudinal axis of the tube, hence the term "spin." However, it is not clear on general hydrodynamic principles why such a rotation should take place. In addition, it develops that these almost horizontal stripes are clearly nothing primary. A photograph taken by Bone, Fraser, and Wheeler<sup>2</sup> with the extraordinarily great speed of Fraser's camera, which fixes the processes in detonation during  $1/10,000$  sec at 25 cm of tube length

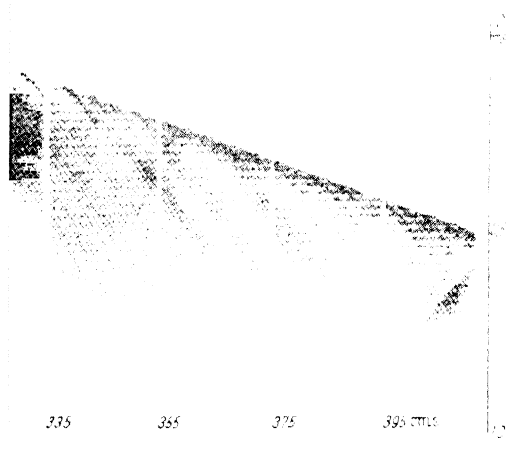


Fig. 125.—Spinning detonation. [From Bone and Fraser, *Phil. Trans. Roy. Soc. London*, A, vol. 230 (1931).]

and which is especially impressive (Fig. 126), shows the following: From the undulating front, paths run obliquely to the fore. These correspond to shining particles that move with a velocity of  $\sim 780$  m/sec. At an angle of  $22^\circ$ , inclined backward against these traces, are paths that correspond to a reverse velocity of  $\sim 320$  m (cf. Fig. 127). These can only be pressure waves in reverse, similar to the detonation wave. They run with only a low velocity, since the medium in which they move is flowing in the opposite direction. The velocity of 780 m forward might be essentially that of the burned gases. The velocity of 1100 m ( $320 + 780$ ) relative to the burned gases is of the order of magnitude of the velocity of sound in the burned gases.

<sup>1</sup> BONE, W.A., and R.P. FRASER, *Phil. Trans. Roy. Soc. London*, A, **230**, 371 (1931).

<sup>2</sup> BONE, W.A., R.P. FRASER, and W.H. WHEELER, *Phil. Trans. Roy. Soc. London*, A, **235**, 29 (1936).

The "frequency" of the spin in  $2\text{CO} + \text{O}_2$  detonation amounts to 148,000 in a tube of 3.62 mm diameter, and to 23,000 with 25.4 mm diameter, in other words, inversely proportional to the diameter of the tube. The "pitch" of the spin is found to be about three times the diameter of the tube.

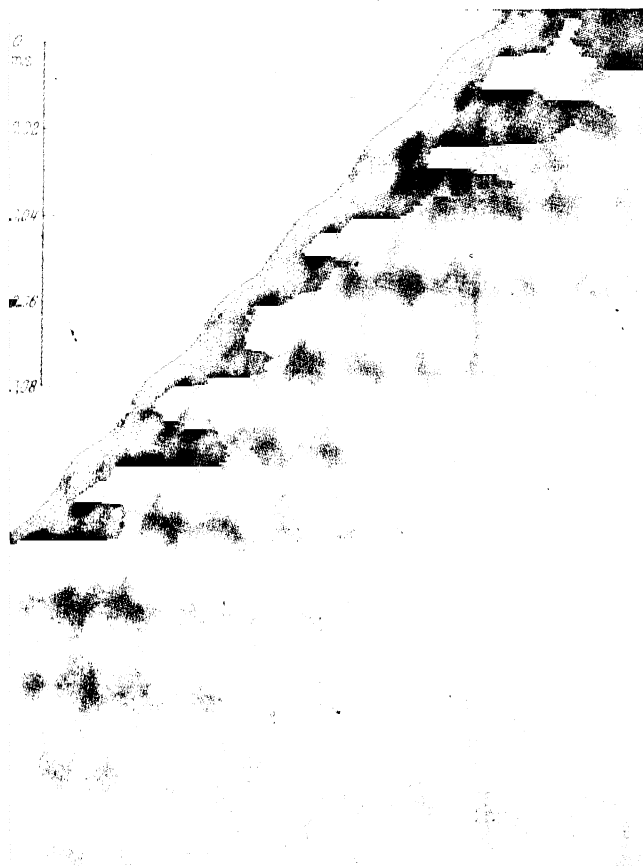


FIG. 126. Photograph of "spinning" detonation. The picture shows the process with a tube length of 25 cm during  $\sim 10^{-4}$  sec. [From Bone, Fraser, and Wheeler, *Phil. Trans. Roy. Soc. London, A*, vol. 235 (1936).]

The last photographs have shown that the original assumption of a rotation of the total gas mass does not necessarily follow. Indeed, the following observations by Bone and Fraser (cited page 193) actually contradict this assumption: If a burr 1 mm in height is placed longitudinally in the detonation tube 12 mm in diameter (Fig. 128), nothing is changed in the spin. Further, Bone, Fraser, and Wheeler (cited

page 193) observed that the spin is preserved in tubes whose cross section is an equilateral triangle, a square, or a right angle. One difficulty remains, however, for the explanation still to be discussed, namely, the spin phenomenon as the rhythmic result of partial explosions. Bone and Fraser (cited page 193) found that spiral fragments appeared in glass tubes through which a "spinning" detonation passed. They further observed<sup>1</sup> that (Fig. 129), in a glass tube through which a detonation passed that had come from a lead tube, a gray precipitate appeared on which was a spiral path with a pitch of 4 cm. Likewise, Bone, Fraser, and Wheeler found that, if the detonation passed through a silver-lined glass tube, the silver had vaporized in a spiral path.

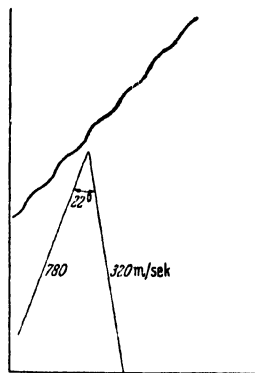


Fig. 127. Sketch of the processes in Fig. 126. Compare the text.

The observations accordingly show that in so-called "spinning detonation" no basis exists for the assumption that the entire detonating gas revolves about the axis of the tube; on the contrary, this assumption may probably be considered as excluded. It seems necessary to conclude that some process connected with detonation, *e.g.*, the place of greatest reaction velocity in the proximity of the wall, propagates in a spiral path.



Fig. 128.

Before we proceed to the explanation of the "spin" phenomenon, we shall concern ourselves with the details of the mechanism of the spontaneous origin of detonation as well as with the introduction of detonation by artificially induced shock waves concerning which work

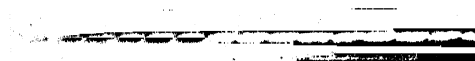


Fig. 129.—Glass tube with lead coating through which a spinning detonation has passed. [From Bone and Fraser, *Phil. Trans. Roy. Soc. London, A*, vol. 228 (1929).]

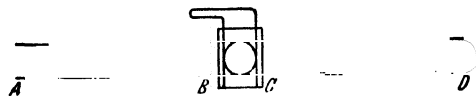


Fig. 130.

has appeared in recent years. These problems have been systematically studied by Bone and Fraser, even though there are many older individual observations. If a shock wave is permitted to affect a plane traveling in the same direction, an acceleration of the flame is always noted.

<sup>1</sup> BONE, W.A., and R.P. FRASER, *Phil. Trans. Roy. Soc. London, A*, 228, 197 (1929).

Experimentally this can be done by connecting the explosion tube *AB* (Fig. 130), which has ignition electrodes at *B*, with a tube *CD* filled with

an inert gas, by means of a pet cock of equal bore. In the latter tube, it is then possible to create a shock wave at *D* by means of either a powerful condenser discharge or a solid explosive. Figure 131 shows a typical experiment. In this case, a shock wave of 760 m/sec was produced at a distance of 2.50 m behind the flame moving at first normally with a velocity of 38.6 m/sec. After  $\sim 3.3 \cdot 10^{-3}$  sec, the flame was overtaken by the shock wave so that its velocity was suddenly accelerated to 308 m/sec. The shock wave (which is naturally not visible on this picture but whose probable course is indicated by the dotted line) now precedes the spontaneously accelerated flame, and the flame tries to overtake the shock wave. Before it is entirely overtaken, auto-ignition takes place at 4.25 cm ahead of the flame front by means of the shock wave. Detonation takes place with a simultaneous reverse "retonation wave." This phenomenon is observed again and again in similar experiments.

The same phenomenon—appearance of detonation ahead of the flame front—is also observed if the detonation is spontaneous without the aid of an independently induced shock wave. In itself this is not surprising, for every flame burning with acceleration (and if a flame does not burn with acceler-

FIG. 131.—Effect of a percussion wave coming from the left (indicated by the dashed line) on a flame (ignited to the left above). (From Bone and Fraser, *Phil. Trans. Roy. Soc. London*, vol. 230.)

ation, it will not change over into detonation) must produce a shock wave ahead of itself which can then have the same effects as an

artificially produced shock wave. This has already been seen on older pictures (Campbell and Woodhead, cited page 192). In Dixon<sup>1</sup> there are photographs that can be interpreted only in this manner. Dixon has already discussed the question of whether the explosion overtakes its own sound wave in such cases.

A particularly beautiful photograph that shows these processes especially clearly and from which an analysis of the individual processes is possible is reproduced here in Fig. 132 and is taken from Bone, Fraser, and Wheeler. The same thing is represented schematically in Fig. 133 with the velocities of the various processes given. In this case, ignition



FIG. 132.—Processes during the origin of a detonation (the flame is coming from the right above). (From Bone, Fraser, and Wheeler, p. 191.)

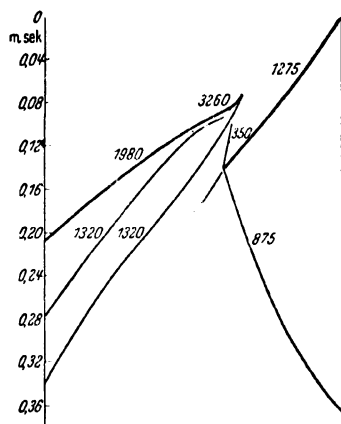


FIG. 133.—Sketch of the processes in Fig. 132 (numbers = velocities in  $\text{msec}^{-1}$ ). (From Bone, Fraser, and Wheeler, p. 191.)

took place at a distance of 6.37 cm in front of the wave front. From the point of ignition, the combustion propagates toward both sides, to the front with a velocity at first of 3260 m/sec, which at the end of the picture has dropped to 1980; and at a further distance it assumes the value of 1760 m/sec, which corresponds to the moist  $2\text{CO} + \text{O}_2$  (to which this picture as well as the others in this section refer). A general observation that can be recognized in most detonation photographs is this: The velocity at the moment of origin can sometimes be considerably greater than in the developed, stationary detonation wave. Connected with this is the fact mentioned earlier, that the pressures in the detonation wave at the moment of origin are also higher than in the stationary condition (page 189). The combustion in Figs. 132 and 133, which progresses

<sup>1</sup> DIXON, *Phil. Trans. Roy. Sci. London*, **200**, 315 (1903).

"backward" from the place of ignition, *i.e.*, toward the original flame front, still has a resulting forward velocity of  $\sim 350$  m/sec as a result of flow. After striking the original flame front, a reverse wave proceeds from there with the velocity of 875 m/sec, which is probably identical with the retonation wave.

The spin in the wave front is fully developed only after the velocity has decreased to that of the stationary detonation. For a further clarification of the processes, Bone, Fraser, and Wheeler have made shadow pictures that show the shock wave by itself shortly before it

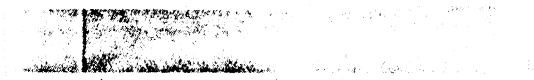


FIG. 134.—Schlieren photograph of a percussion wave. (From Bone, Fraser, and Wheeler, p. 191.)

is overtaken by the flame, and also the disturbed wave front overtaken by the flame (Figs. 134 and 135). On the basis of various experiments, they give the schematic presentation of the origin of a detonation shown in Fig. 136. From above to below, Fig. 136 shows the various successive stages. *BB* is the shock wave; *A* is the flame following it with a velocity of 1275 m/sec. At 4, ignition has taken place in the shock wave. The following stages cannot be interpreted entirely satisfactorily. At any rate, the regular front forms by the union of shock wave and burning

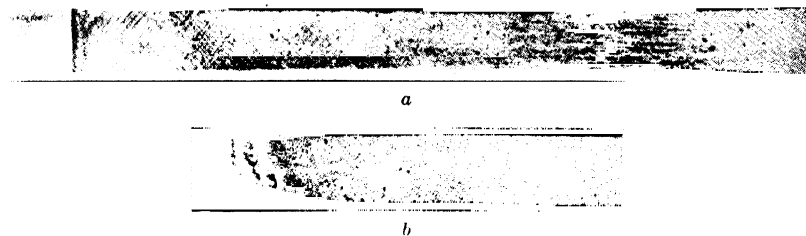


FIG. 135.—*a*. Percussion wave; flame front to the right. *b*. Percussion wave and flame front close together with mutual disturbances. (From Bone, Fraser, and Wheeler, p. 191.)

zone. Bone, Fraser, and Wheeler assume that the burning zone ends toward the front in a point, whose course on the periphery represents the spin. The authors explain the movements indicating the presence of individual partial explosions directed forward and backward, which are connected with every "wave" of the spin (Figs. 126 and 127) in the following manner: The spinning of the point of the burning zone causes a pocket of unburned gas to remain behind at every half turn for geometrical reasons; this pocket of gas then suddenly burns. This explanation for spin does not seem to be proved in detail by the experiments. In its favor is the fact that it embraces all the phenomena.

On the other hand, the explanation for spin provisionally given by Becker<sup>1</sup> does not account for the paths observed on the wall of the tube, but for the rest it adapts itself completely to the experimental and theoretical findings thus far obtained. Just as in the extreme example of Fig. 132 ignition has taken place far ahead of the flame front, so combustion in the normally developed detonation wave can, though less pronouncedly, be extinguished rhythmically and again be ignited by the shock wave, which continues even without combustion. Although we

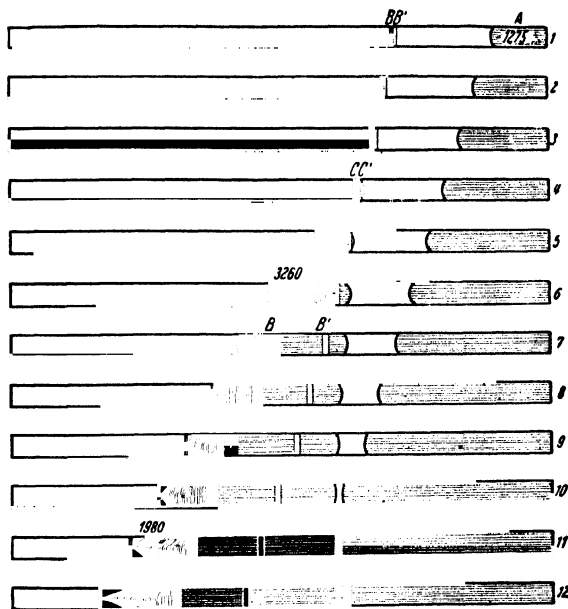


FIG. 136.—Sketch of the origin of a detonation. Numerical values = velocities in  $\text{msec}^{-1}$ . (From Bone, Fraser, and Wheeler, p. 191. Compare the text.)

have assumed a firm union of shock wave and burning zone as the ideal case in the theoretical treatment of detonation, both must here be accorded a certain independence. Shock wave and burning zone can separate and then unite again. For this process, a considerable number of direct experimental proofs can be furnished. It is possible, for example, to extinguish the detonation by means of a suitable external field, while the shock wave continues on its way, followed by a flame. A longitudinal electrical field, for instance, which was so directed that the flame produced ran from negative to positive, effected at a strength of 5000 volts/cm a deceleration of the flame to a maximum of 800 m/sec.

<sup>1</sup> BECKER, R., *Z. Elektrochem.*, **42**, 457 (1936).



To a magnified degree, the process to which Becker attributes spin is demonstrated in an experiment by Bone, Fraser, and Wheeler (cited page 193) in which a moist mixture of  $2\text{CO} + \text{O}_2$  was detonated in a

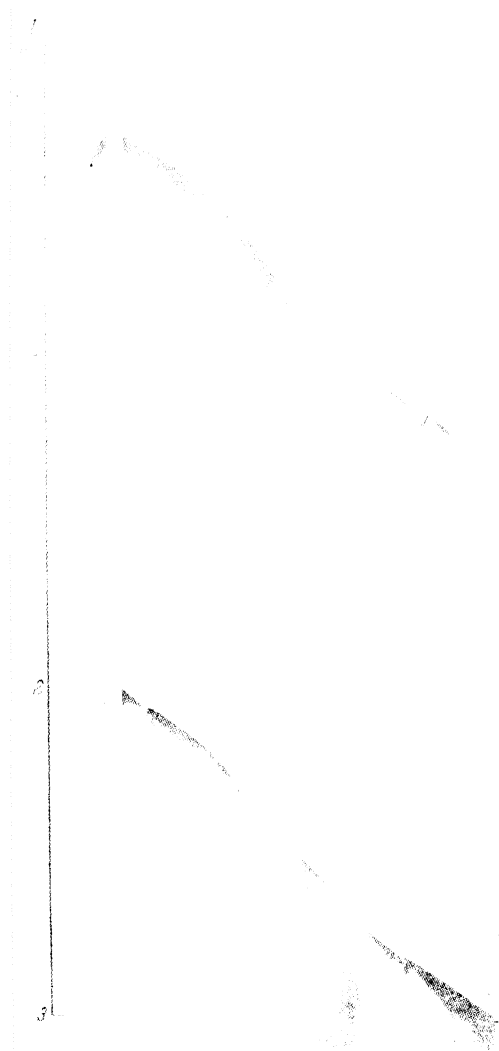


FIG. 137.—Photograph of the detonation of  $2\text{CO} + \text{O}_2$  in a tube 3.62 mm in diameter. The lower part of the picture shows the continuation of the process pictured in the upper part. (From Bone, Fraser, and Wheeler, p. 191.)

tube of only  $\sim 3.62$  mm in diameter. This is very close to the lower limit of diameter at which detonation is propagated at all. In Fig. 137, a photograph is reproduced that shows this process. There is, first of

all, a flame velocity of 1225 to 1230 m/sec. Then detonation appears in front of the flame front with an initial velocity of 1840 to 1860 m/sec, which decreases to 1760 m/sec. Thereupon the flame decelerates quickly to from 1155 to 1160 m/sec. At the same time, the shock wave apparently runs ahead of the flame with similarly decreasing velocity. About 80 cm from the first detonation, the shock wave has decelerated to such an extent that it is overtaken by the flame, and a new detonation therefore takes place ahead of the flame front. Without a doubt, the exact process which Becker suggests for spin is duplicated, except that in a narrow tube the entire phenomenon takes place very slowly.

If the explanation for spin suggested by Bone and Fraser were correct, it should be possible to observe the spin in a similar manner for all gas mixtures that detonate. In reality, however, spin is most pronounced in carbon monoxide (in all detonating mixtures with  $O_2$ ), and in some methane, ethane, ethylene,  $CS_2$ , and in  $C_2N_2$ -oxygen mixtures. Spin is not shown in  $H_2$ - $O_2$  mixtures (at least, not by the photographic methods hitherto developed). On the other hand,  $H_2$ -air mixtures show spin in the neighborhood of the detonation limits.<sup>1</sup> That mixtures difficult to detonate (like  $2CO + O_2$ ) as well as mixtures in the neighborhood of the detonation limits show spin especially well seems not to exclude the possibility that a not sufficiently rapid reaction velocity and therefore a possible separation of shock wave and combustion are actually the cause of spin (cf. in this connection page 206).

#### 9. Supplementary Material to the Theory of Detonation Processes.—

The relations derived above for shock waves [Eqs. (10) and (11)] represent expressions that would result from a strict application of hydrodynamics.<sup>2</sup> The simple formal theory represents the shock wave as an unstable surface in which fresh gas and exhaust gases are side by side. The idea of the wave front as an unstable surface, is of course, only a mathematical abstraction. If we introduce the influence of heat conduction and internal friction, we obtain instead a continuous transition, which, to be sure, can take place in a very short distance under certain circumstances. Becker (cited page 163) has made computations that take into account conduction and viscosity and has thus obtained relations for the frontal extent of the shock wave. In detonation, diffusion would normally have to be taken into account, just as it would in ordinary flames, since the reaction, even in the detonation wave, can be furthered by the diffusion of free atoms and radicals (cf. the stationary concentrations of H and OH in the oxygen-hydrogen detonation computed by

<sup>1</sup> Cf. FRASER, R.P., "The Science of Petroleum," quoted p. 163.

<sup>2</sup> For a detailed theoretical treatment of the origin of a compression stroke, cf. R. Becker, *Z. Physik*, **8**, 321 (1922); also E. Bollé, "Handbuch der physikalischen und technischen Mechanik," Vol. VI, 1927, quoted p. 163.

Lewis). It is at any rate of interest to know the order of magnitude that results for the frontal width of explosion waves. For air, at atmospheric pressure and 0°C, Becker computes the following widths for various percussion pressures  $p_2$ :

|   |     |     |    |      |      |      |      |
|---|-----|-----|----|------|------|------|------|
| $p_2 = (\text{atm}) \dots\dots\dots$                    | 2   | 5   | 10 | 100  | 1000 | 2000 | 3000 |
| Front width $l \times 10^7 \text{ cm.} \dots\dots\dots$ | 447 | 117 | 66 | 16.5 | 5.2  | 3.6  | 2.9  |

For the pressures, which come into consideration for detonation waves, the frontal width is accordingly of the order of magnitude of the free length of path. To be sure, the values computed for an explosion wave cannot be directly applied to the somewhat different conditions actually in the detonation wave.

We must treat more in detail the question of the stability of the detonation wave. We must clarify whether the point *I* on the Hugoniot-curve (Fig. 116) actually represents a distinct condition of stationary detonations. We have already found (page 171) that the detonation velocity or the burned gas velocity is given by

$$D = v_1 \sqrt{\frac{p_2 - p_1}{v_1 - v_2}} = v_1 \sqrt{\tan \alpha}$$

$$W = (v_1 - v_2) \sqrt{\frac{p_2 - p_1}{v_1 - v_2}} = (v_1 - v_2) \sqrt{\tan \alpha}$$

We have further seen that no real importance is attributable to the branch *GF* of the Hugoniot-curve and that the branch *FK* must correspond to ordinary combustion. However, all velocities are possible for detonation that correspond to terminal conditions on the branch *GDIB*. An infinitely great detonation velocity would be attributable to the point *G* corresponding to a momentary combustion of the total gas at constant volume. For reasons of kinetics, that solution is impossible. It is to be expected at the outset that points in the neighborhood of *G* do not come into consideration as a terminal condition. The point *I* is unique because it produces the smallest detonation velocity possible, to which, in addition, only a single terminal condition of the gases pertains, since for all other velocities there are two different possible conditions. For example (Fig. 116), the same detonation velocities pertain to the points *D* and *B*.

It can be shown that, in point *I*, entropy is at a minimum, whereas it reaches a maximum in the lower contact point *K* on the combustion branch (point *K* is for our purpose of no special importance). That the entropy at point *I* assumes an extreme value can best be illustrated from Becker in the following manner: If we designate the internal energy at *B* as a terminal condition by  $E_2$  and correspondingly that proper

to  $D$  by  $E'_2$ , while the energy  $E_1$  is assigned to the initial condition  $A$ , then the Hugoniot-equation is valid.

$$\begin{aligned} E_2 - E_1 &= \frac{1}{2}(p_1 + p_2)(v_1 - v_2) \\ E'_2 - E_1 &= \frac{1}{2}(p_1 + p'_2)(v_1 - v'_2) \end{aligned}$$

As can be seen from Fig. 116, the right sides represent the surfaces of the trapezoid  $ABB'A'$  and  $ADD'A'$ . Hence the following is also valid:  $E_2 - E'_2$  = the surface of the trapezoid  $DBB'D' = \frac{1}{2}(p_2 + p'_2)(v'_2 - v_2)$ . Now the following is valid for the integral taken in the direction of the straight line  $DB$ :

$$\uparrow \int_D^B T dS = \int_D^B dE + \uparrow \int_D^B p dv = E_2 - E'_2 - \text{Surface } DBB'D'$$

hence

$$\uparrow \int_D^B T dS = 0 \quad (18)$$

If  $D$  and  $B$  are moved together infinitely, this changes into

$$dS = 0$$

that is, this is valid for the tangent drawn from  $A$  to the curve. At  $I$ , the Hugoniot-curve is touched by the curves  $S = C$ , that is, the adiabatics. Equation (18) can clearly be fulfilled only if  $T dS$  changes its sign in proceeding from  $D$  to  $B$ . This means that, at a point lying between  $D$  and  $B$ , the adiabatic passing through this point is touched by the straight line  $DB$ . If one imagines the curves  $S = \text{const}$ , i.e., the adiabatics, drawn in, then the latter must be steeper at  $B$  (above  $I$ ) than the straight line  $DB$ , and at  $D$  (below  $I$ ) they must be less steep than this straight line. If one designates the slope of the adiabatics with  $\varphi$ ,

$$\varphi = - \left( \frac{dp_2}{dv_2} \right)_{\text{ad}}$$

while the slope of the straight lines is given by

$$\tan \alpha = \frac{p_2 - p_1}{v_1 - v_2}$$

then the following is valid: Above  $I$ ,  $\varphi > \tan \alpha$ ; below  $I$ ,  $\varphi < \tan \alpha$ .

Now the speed of sound in the burned gases is<sup>1</sup>

$$\lambda = v_2 \sqrt{- \left( \frac{dp_2}{dv_2} \right)_{\text{ad}}} = v_2 \sqrt{\varphi}$$

A rarefaction wave appearing in the burned gases and progressing with the velocity of sound can overtake the detonation and weaken it if the velocity of sound in the burned gases + the velocity of the burned gases > the detonation velocity, or if

$$v_2 \sqrt{\varphi} + (v_1 - v_2) \sqrt{\tan \alpha} > v_1 \sqrt{\tan \alpha}$$

<sup>1</sup> The value for the velocity of the sound  $\lambda$  (wave with vanishing amplitude) can easily be obtained from the above equation for  $D$  for the borderline case  $(p_2 - p_1) \rightarrow 0$

$$\lim_{(p_2 - p_1) \rightarrow 0} D = v \sqrt{- \frac{dp}{dv}} = \lambda$$

As long as this unbalanced equation existed, the detonation would be unstable. Since, above  $I$ ,  $\varphi > \tan \alpha$ , it follows that also above  $I$  the detonation wave is mechanically unstable. At the point  $I$ ,  $\varphi = \tan \alpha$  and exactly there, as we have mentioned on page 170, the detonation velocity is equal to the sum of the velocity of the burned gases plus the velocity of sound in the burned gases. Let us therefore assume that the detonation had been induced with a velocity corresponding to the transition at point  $B$ . Then the detonation wave will be weakened by the rarefaction wave following it, and its velocity will drop until it corresponds to the point  $I$  where the rarefaction wave can no longer overtake the detonation wave and accordingly cannot further weaken it. Actually the velocity of the detonation at its origin is often above the stationary velocity but soon drops to the latter value.

This demonstrates that detonations corresponding to points above  $I$  are unstable and that toward this branch of the Hugoniot-curve the point  $I$  corresponds to the stable detonation velocity. We have already seen that the branch  $IG$  in the neighborhood of  $G$  can correspond to no real process. It remains to be shown that the rest of the points below  $I$  also do not come into consideration for a stable detonation.

We have seen that the following is valid for the conditions  $D$  and  $B$ :

$$E_2 - E'_2 = \frac{1}{2}(p_2 + p'_2)(v'_2 - v_2)$$

That is, the same relation exists between the two conditions as exists

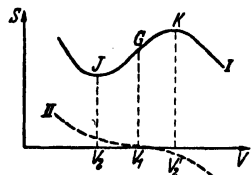


FIG. 138.—The points  $I$ ,  $G$ ,  $K$  correspond to the same points in Fig. 116. The designation of the volumes is different from Fig. 116. (From R. Becker, p. 161. Compare the text.)

between the initial and terminal condition in an ordinary compression stroke. Accordingly, a greater entropy must be accorded point  $B$  than point  $D$ . If we therefore assume that the burned gases at the moment of their origin change over into the condition of greatest probability, then in a given case not point  $D$  but instead point  $B$  would be reached. Since a detonation corresponding to point  $B$  is unstable, however, the transition to point  $I$  would take place as observation shows.

That entropy at  $I$  has an extreme value ( $dS = 0$ ) has been shown; that it actually assumes a minimum, in other words,  $\left(\frac{d^2S}{dv^2}\right)_H > 0$ , is proved in Becker, for instance (cited page 163). For purposes of illustration, we add a representation for the change in entropy as a function of  $v$  along the Hugoniot-curve, which is taken from Becker (Fig. 138). Under it, the corresponding curve for an ordinary compression stroke is represented. In place of a maximum and minimum, only

a turning point appears with a horizontal tangent at the  $S$  curve. The points  $I, G, K, v_2$  and  $v'_2$  all coincide with the point  $v_1$ .

The above condition of the touching of the Hugoniot-curve and the adiabetic at the point  $I$  yields the additional equation (already introduced on page 170) for the computation of the detonation velocity

$$\frac{p_2 - p_1}{v_1 - v_2} = - \left( \frac{dp_2}{dv_2} \right)_{ad}$$

Perhaps it would be profitable to consider an objection that might be raised: Does a rarefaction wave really follow the detonation wave, and should the condition of mechanical instability above  $I$  really be taken into account? Against this objection, it can be pointed out that a rarefaction wave must always form at some distance behind the wave front under the usual conditions of a detonation even if the effect of cooling is disregarded; for we have already seen above (page 172) that the pressure in the burned gases will decrease toward the rear and that the original forward-directed movement of the burned gases must accordingly be decelerated and then reverse. This can be directly demonstrated by detonation pictures (Fig. 139). The photograph of a spinning detonation taken by Bone and Fraser shows the forward-directed paths of the burned gases, but these at first take a straight course, then reverse with a deceleration amounting to almost a static condition. Beyond that the trace cannot be followed because the luminous power is no longer great enough. In Dixon's works, there are photographs that follow the traces considerably farther, showing a complete reversal of the original velocity of flow of the burned gases. In Fig. 140, this is schematically portrayed. There can thus be no doubt that the conditions for the origin of a rarefaction wave behind the wave front are always present insofar as the above way of preserving the stability conditions is justified.

It is important to understand how the reaction in the front of the

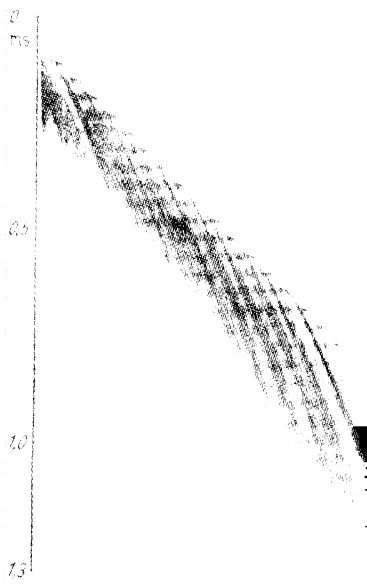
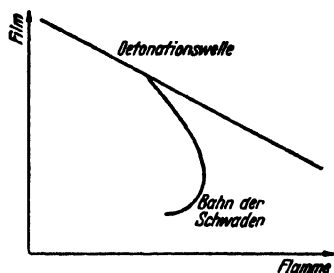


FIG. 139.—Detonation photograph. It shows the bending of the paths (directed to the right and downward) of the burned gases. (From Bone and Fraser, *Phil. Trans. Roy. Soc. London*, vol. 230.)

detonation wave takes place<sup>1</sup> and how great the velocity of the chemical reaction must be.

For the first, it is almost self-evident that the velocity of the chemical conversion must keep pace with that of the progress of the wave front. It can further be assumed that the "thickness" of the wave front must be of the order of magnitude of a free length of path.<sup>2</sup> Only thus is it easy to understand that the energy liberated in conversion is transferred to the wave front by shocks and is thus made serviceable to the preservation of the shock wave.

Here, however, a peculiar difficulty appears. The detonation velocity



(Detonationswelle = detonation wave  
Bahn der Schwaden = path of the  
burned gases  
Flamme = flame)

FIG. 140.—Sketch of the bending of the path of the burned gases according to older photographs by Dixon, p. 159.

This fact is of decisive importance especially for the detonation of solid explosives.<sup>1</sup>

However, even after all this has been taken into consideration, the output factor, even in the most favorable reactions, like that of oxygen-hydrogen combustion, for example, is considerably lower than unity, and actually is decreased by the probable presence of spatial factors. Especially in the oxygen-hydrogen reaction, extraordinarily high H-atom and OH-radical concentrations appear in the detonation wave (see page 174). If the reaction lags behind the wave front by only a little, however, this high concentration is not available in the wave front.

Considerably more unfavorable are the conditions in reactions that are inconceivable without the decisive participation of triple collisions, as, for example, in carbon monoxide combustion; and conditions are most unfavorable of all in the combustion of more complicated organic

<sup>1</sup> Cf. in this connection LEWIS, B., *J. Am. Chem. Soc.*, **52**, 1320 (1930). He proceeds from a statement of the problem which has since been abandoned. Also JOST, W., *Z. Elektrochem.*, **41**, 191 (1935). For solid explosives, cf. Schmidt, A., *Z. ges. Schiess- u. Sprengstoffw.*, 1935–1938

<sup>2</sup> Cf. the computations by Becker for shock waves, p. 163.

is approximately as great as the velocity of the thermal movement in the burned gases; but, if the reaction is to keep pace with the progress of the wave front, there would have to be a reaction at almost every collision of the molecules or at least in a great portion of the collisions. To be sure, the reaction in the wave front is furthered by the fact that, in addition to the subordinated thermal movement, the energy of the directed flow of the burned gases against the fresh gas is available as activating energy (this energy is of the same order of magnitude as the average thermal energy).

molecules and in the disintegration of solid explosives. The transition from a complicated molecule with perhaps over 20 atoms to the corresponding terminal condition cannot be imagined without the participation of a large number of collisions. If all this is taken into consideration, the problem is obviously not to find a mechanism that permits the chemical reaction to keep pace with the front of the shock wave, but rather to understand how a stationary detonation occurs, although the chemical conversion cannot in principle be completed in the wave front itself.

In the theory of detonation velocity, it is, to be sure, not expressly assumed that the reaction terminates in the wave front; indeed, the processes in the wave front are entirely excluded from consideration. The assumption is, however, implicitly contained in it that the reaction energy can be utilized in the wave front. The formal introduction of the wave front as an unstable surface would even demand that the reaction take place in an extremely short time. It is possible to obviate the above difficulty by proceeding from a peculiarity of the theory of detonation velocity. We have shown (pages 202ff.) that only the detonation velocity corresponding to the point *I* of the Hugoniot-curve (Fig. 116) comes into consideration as a stationary detonation velocity.

The manner of proof is convincing and yet permits a peculiar situation to exist: If we imagine the condition corresponding to the stationary detonation velocity as displaced by means of a small disturbance from the point *I* in the direction of *B*, then it follows from the above considerations, since it must be in stability, that the condition will of its own accord return to *I*. In a displacement of *I* in the direction of *D*, we can see the same thing, but only very indirectly. In a displacement up to *D*, it follows only that the condition *B* belonging to the same detonation velocity is more probable, and on its part would then pass over to *I*. Clearly, however, it must be possible to show that, in a displacement of *I* in the direction of *D*, either this displacement is reversed of its own accord or no possible wave can correspond to the branch *IDG*. For the terminal point *G*, this can be seen without difficulty. Infinite detonation velocity without a change of volume would correspond to it, *i.e.*, the reaction would spread more rapidly from some spot than the change in volume could follow. Since the velocity always remains finite with the finite temperatures that come into consideration, this process may be excluded.

By this, we are led to think of an influence of the reaction velocity also for the instability of the section between *I* and *G*.<sup>1</sup> We suspect that, with finite reaction velocity, the branch *IDG* is unstable.<sup>2</sup>

<sup>1</sup> Cf. Jost, W., *Z. physik. Chem.*, Sec. B, **42**, 136 (1939).

<sup>2</sup> In these considerations, use should be made of the fact that the reaction velocity is finitely great and not infinitely great. All considerations that make use of a special



Let us observe the detonation wave belonging to point *D*. In point *D* (*cf.* page 203), the sum of sound velocity plus flow velocity of the burned gases is smaller than the detonation velocity. Since, with finite reaction velocity, the reaction energy is entirely liberated only at a certain distance behind the wave front, this energy can no longer be furnished the wave front. The detonation wave is therefore weakened because the reaction energy cannot be furnished to it and its velocity decreases.

Above *J*, the energy liberated behind the wave front could be directly transferred to it, but this range does not come into consideration for the reasons given above. It still remains to be considered whether in *I* itself the reaction energy can be transferred to the wave front. This is in itself possible; for, since a sound wave that would originate behind the wave front would accompany the latter at a constant distance, every compression wave with greater amplitude that moves with a velocity

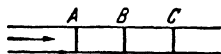


FIG. 141.

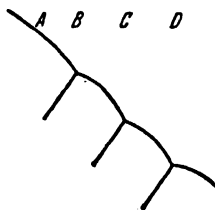


FIG. 142.

greater than sound must overtake the wave front. Even though little energy is liberated and the wave velocity is only a little above the velocity of sound, a wave could overtake the front, which does not come into consideration for points between *I* and *G*.

This shows, to be sure, that a transference of the reaction energy to the wave front at *I* (at not too low a reaction velocity) is possible; but, since use has been made of the spreading process of a wave, it has not been shown whether, under these circumstances, a completely stationary condition can appear. This would demand a very thoroughgoing examination.

However, the following thought suggests itself: Instead of assuming that the reaction is continuous, let us observe the simple borderline case of a completely discontinuous reaction (Fig. 141). Let the wave front meet the fresh gas at *A* and let a certain distance to *B* be traversed before lively reaction between *A* and *B* takes place. Since, during this period, no delivery of energy has taken place, the shock wave must have been weakened and decelerated (Fig. 142). Now the reaction between *A* and *B* has taken place rather suddenly. From the place of reaction,

---

reaction mechanism and special numerical values of the reaction velocity should be excluded in the framework of the thermodynamic-hydrodynamic theory.

waves proceed forward and backward, of which one delivers energy to the front of the shock wave and accelerates it, while the other must be visible as a reverse wave (Fig. 142). In the meantime, the wave front has traversed the section  $BC$ , although reaction did not take place in it. The wave is again decelerated, and again sudden reaction and a renewed acceleration of the wave takes place. The view that we have given here corresponds rather precisely to that observed in spinning detonation (*cf.* Fig. 126). Our observations differ from similar considerations by Becker (cited page 199) in the fact that the point of departure is a different one and in the fact that we consider new ignition not in the front of the shock wave but in the section already traversed by the shock wave, as reaction-kinetic considerations suggest. On the basis of these observations, we should expect that the distance  $AB$  that must be traversed by the wave front until lively reaction takes place is longer in proportion as the mixture is sluggish in reaction. This appears to correspond very well to experimental findings (*cf.* page 200).

## CHAPTER VI

### FLAMES OF GASES NOT PREMIXED

It is our aim essentially to present the processes in the ignition and combustion of explosive mixtures. In so doing, we have come upon a group of conversions in the detonation processes in which the velocity of the chemical reaction no longer plays a role. Its magnitude determines only whether detonation takes place or not. As long as we restrict ourselves to the action of premixed gases, in other words, to the action of an explosive mixture, these are the only processes independent of the reaction velocity. In actual practice, however, in a considerable group of combustion processes, the combustion velocity is not determined—or at least not predominantly determined—by the reaction velocity. This is the case in the combustion of gases not premixed, examples of which are the ordinary candle flame, the illuminating-gas flame, the combustion in the outer ring of the Bunsen flame, and all technical combustions with gases not premixed. Such combustions are important either if we need a definite atmosphere above the material to be heated, *e.g.*, a reducing atmosphere in the Siemens-Martin furnace, or if we place special value on the highest possible radiation at not too high temperatures. For this purpose, the flame of gases not premixed and with carbon elimination in the range of excess fuel is especially favorable. In such cases, the reaction velocity of the flame is of subordinate importance as long as the temperature of the flame is high enough. What determines the velocity of the combustion in this case is the *mixing process*.

For mixing, diffusion is one of the first considerations. In technical combustion on a large scale, the conditions for mixing by diffusion alone are no longer given; for only by laminar flow could mixture exclusively by diffusion occur even at greater layer thicknesses. Under the conditions of technical combustion, however, we must generally, if not always, reckon with turbulence. Even though a discussion of these processes may lead somewhat beyond the limits of the processes treated in this book, we shall, because of the technical value of the subject, at least give a survey of the subject. We follow Rummel,<sup>1</sup> who is chiefly responsible for clarifying these relations.

Even though these processes have a special type of firing for their object, they nevertheless show especially clearly the importance of

<sup>1</sup> RUMMEL, K., "Der Einfluss des Mischvorganges auf die Verbrennung von Gas und Luft in Feuerungen," Verlag Stahleisen, Düsseldorf, 1937.

turbulent mixture, which surely can be of importance in other cases too, though it has not always been accorded sufficient attention.

We shall first regard a more simple individual case, a burner of small dimensions with laminar flow and mixture exclusively by diffusion. This case has been treated theoretically by Burke and Schumann,<sup>1</sup> but with considerable simplifications. Let us imagine a cylindrical burner of such construction that the fuel gas is furnished from an inner tube of the radius  $r$  while the fresh gas flows from a wider concentric tube of the radius  $R$  (Fig. 143). In order to make a simple theoretical treatment possible, we must assume that the velocity of flow of gas and air are the same and are also constant over the entire cross section, in other words, that the conducted masses of air and gas are to one another as the cross sections of the tubes, as  $(R^2 - r^2)/r^2$ . If we ignite such a system above the mouth of the inner tube, a stationary flame can form above it with suitable flow conditions. This flame, assuming sufficient air supply, might correspond to the form of a free-burning candle<sup>2</sup> or a luminous gas flame. With excess air, this flame has approximately the form shown in Fig. 143a. If its height is designated by  $y$ , a further diffusion will take place above  $y$ , and this diffusion would be of such a nature that the air content in the center, which is equal to zero at point  $y$  where the combustion would be complete, continuously rises to a terminal value. If no excess of air is present, no mixture with excess air results as a terminal gas. Thus, just as in the preceding case the range of the terminal gases was obtained by widening the range of the fresh air, so the range of the terminal gas in this case must be obtained by widening the range of the fresh gas. In other words, a burning zone of the kind shown in Fig. 143b must be expected. Experiments show that, also in the case of diffusion flames, we obtain a thin burning zone that can be described as approximately plane.

It is possible to treat these and similar diffusion problems (e.g., the case of the "plane" flame in Fig. 144) quantitatively and thus to compute the form of the burning surface as well as the height of the flame. For further details, see Burke and Schumann as well as Lewis and v. Elbe.<sup>1</sup>

Except for the computation of the flame form, it is possible to arrive at the proper conclusions by means that are considerably more elementary

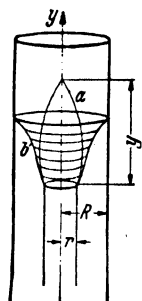
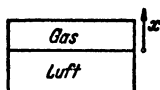


Fig. 143.—  
Diffusion  
flames. Fuel  
flowing in the  
inner tube, air  
in the outer  
tube. a. Flame  
with excess air.  
b. Flame with  
excess fuel.  
(From Burke  
and Schumann.)

<sup>1</sup> BURKE, S.P., and T.E.W. SCHUMANN, *Ind. Eng. Chem.*, **20**, 998 (1928). Cf. also LEWIS and v. ELBE, "Combustion, Flames and Explosion of Gases."

<sup>2</sup> The candle flame differentiates itself from the above-treated diffusion flames by the further fact that the fuel is first vaporized by the heat from the burning zone.

than those which were employed by Burke and Schumann. However, since their computations have been made with considerable simplifications, which will be discussed later, the results of our simpler method should produce about the same degree of accuracy as theirs. The simplifications of which Burke and Schumann made use, in addition to those already mentioned, are as follows: The velocity of flow and the coefficient of diffusion are assumed to be constant along the entire flame, although both can increase in the interval of initial to terminal temperature by about five to ten times. The errors thus introduced compensate each other to some extent, to be sure; for the increase in flow velocity



(Luft = air)

FIG. 144.

with the rising temperature tends to draw the flame out lengthwise, whereas the simultaneous increase of the diffusion coefficient has the opposite effect. An exact compensation cannot be reached, since  $v$  increases with the temperature in inverse proportion to the densities of the gas, while  $D$  must increase considerably, since it already rises at constant density with a power of  $T$  lying at least between  $\frac{1}{2}$  and 1. As a second simplification, it is assumed that the diffusion takes place only perpendicularly to the direction of flow,<sup>1</sup> for only thus does one obtain a simple radial symmetrical or one-dimensional diffusion problem. Since the burning surface is noticeably inclined toward the direction of flow, this assumption too is fulfilled only approximately, but only negligible errors could result. Finally, all these considerations naturally do not hold for turbulence.

We therefore content ourselves with the following consideration: The height of the flame  $y$ , will be given by the fact that, at the place at which the flame ends, the average depth of penetration of air in gas by diffusion must be about equal to  $r$  (Fig. 143), and that of gas in air must be equal to  $R - r$ . In order to estimate the depth of penetration  $x$ , we employ the formula of the average square of displacement

$$x^2 = 2Dt \quad (1)$$

in which we substitute  $x^2$  for  $r^2$  as an approximation. If we now disregard the same entities that Burke and Schumann disregarded, we can state (Fig. 143), if  $v$  is the velocity of flow of gas and air,

$$r = \frac{y}{t}, \quad t = \frac{y}{v} \quad (2)$$

Here  $t$  is the time the gas needs to flow from the mouth of the burner to the tip of the flame at  $y$ , in other words, also the time that is available for

<sup>1</sup> Since in laminar flow the velocity of the flow is not constant over the entire cross section, a diffusion perpendicular only to the direction of flow is out of the question.

diffusion as a whole. If (2) is combined with (1),

$$x^2 = 2D \frac{y}{v}; \quad y = \frac{vx^2}{2D} \quad (3)$$

From this, it is possible to read right off what follows from the complicated result of Burke and Schumann:

1. The height of the flame  $y$  remains unchanged if the burner dimensions are enlarged in the ratio  $m$  (in other words, if we write  $mx$  instead of  $x$ , and at the same time keep the increased volume constant, while the linear flow velocity decreases to  $v/m^2$ ). From (3), it follows that  $y$  then retains its original value.

2.  $y$  must change in the opposite manner from  $D$ . A comparison shows that the flame height of a carbon monoxide flame is to that of the corresponding hydrogen flame about as 2.5 to 1, whereas the diffusion coefficients at room temperature are about in the ratio 1:4.

3. If the fuel gas of a flame with excess air is replaced by an inert gas, the flame must get shorter because now less oxygen needs to diffuse into the fuel gas than before. A quantitative relation for this cannot be derived from (3). Conversely, a flame with lack of air must become longer (Fig. 143) if a part of the fuel gas is replaced by an inert gas, because the concentration gradient for the fuel gas diffused into the air is now correspondingly smaller.

4. If other factors are constant,  $y$  is directly proportional to the flow velocity  $v$  (Table 41).

TABLE 41.—GAS VELOCITIES AND HEIGHTS OF DIFFUSION FLAMES (FROM BURKE AND SCHUMANN)

| Liters of<br>air per hour | Liters of<br>methane per hour | Flame<br>height, cm | Flame height divided by the<br>volume of flow of methane |
|---------------------------|-------------------------------|---------------------|--|
| 198                       | 10.7                          | 3.1                 | 0.29   |
| 382                       | 21.2                          | 8.6                 | 0.405  |
| 509                       | 28.3                          | 11.3                | 0.40   |
| 573                       | 37.1                          | 14.8                | 0.40   |
| 835                       | 46.4                          | 18.4                | 0.396  |
| 1050                      | 58.4                          | 22.9                | 0.392  |
| 1160                      | 64.6                          | 25.1                | 0.389  |

We can also attempt to measure the absolute height of the flame. Considering the great simplifications in computation, we can expect no more than an agreement to the extent of the order of magnitude. If a better agreement actually is obtained, it may be regarded as chance.

Burke and Schumann, for example, obtained a flame height of 3.3 cm for a flame burning with excess air at  $r = 1.27$  cm,  $R = 2.54$  cm, and with

$v = 1.55$  cm/sec as well as  $D$  (at room temperature)  $\sim 0.5$  cm<sup>2</sup>/sec. If we use (3) for purposes of estimation, we obtain with the same numerical values, in other words,  $x = 1.27$  cm,

$$y = 1.55 \cdot \frac{1.27^2}{(2 \cdot 0.5)} = 2.5 \text{ cm}$$

which is a satisfactory agreement and is well in accord with the results of experience.

If we now take an extreme example, as often occurs in industrial combustion, let us say,  $x = 5$  cm,  $v = 10^3$  cm/sec, and if we retain the same value for  $D$ , then,

$$y = \frac{10^3 \cdot 25}{1} = 250 \text{ m}$$

which far exceeds the dimensions of the furnaces. Even if we consider that the jet of gas in technical combustion is not enclosed in an outside

tube and can thus spread to the side, resulting in a lower velocity than at the exit, the conversion times or paths obtained are still far too long. Technically this would mean that an extremely inefficient use of the fuel gas would take place inside the actual furnace. In reality, such long burning periods, 25 sec in the above instance, are not necessary. One-tenth of this suffices. The mixing process in these technical combustions must thus take a different course. A complete mechanical mixing is obviously out of the question. However, gas and air can be quite thoroughly mixed by turbulence, and the remaining gas and air fields are then so small that the mixing still to be done can easily take place by diffusion in the time remaining. If, for example, the thickness of the layer of the individual air or gas fields were reduced by turbulence from the original 5 to the value of 1 cm, the time needed for diffusion would be reduced to  $1/25$ . It is thus clear that the small turbulence caused by flow is sufficient to accelerate the mixing process considerably.

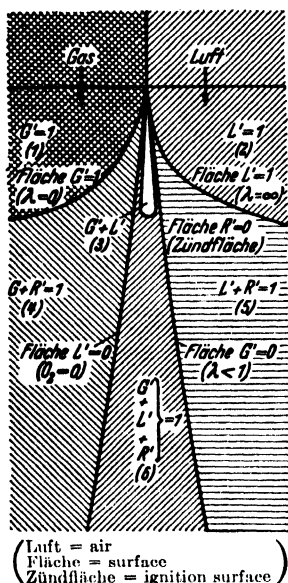


FIG. 145.—Sketch of firing with gases not premixed. Compare the text. (From Rummel, p. 208.)

For a given technical combustion, it is important that practically complete conversion takes place in the actual combustion chamber in order to avoid losses. It might further be demanded that a lack of air prevail in the neighborhood of the reaction material in the furnace in

order that no iron will burn off, *e.g.*, in the Siemens-Martin furnace. This means that an additional demand is made on the mixing process in the combustion chamber.

In order to illustrate the conditions in combustion, it is necessary to show the spatial division of the reacting materials (as it can be determined by tests taken at various points by means of probes and chemical analysis). In this procedure, it is advisable, according to Rummel, not to give the results of the analysis (percentage of  $\text{CO}_2$ ,  $\text{O}_2$ , etc.)<sup>1</sup> but to compute back from these to the portion of "unburned gas"  $G'$ , air  $L'$ , and "reaction gas"  $R'$ , in which the prime indicates that all this refers to the moist component. In this manner, we obtain the schematic presentation of the conditions in combustion shown in Fig. 145.

Air and gas are emitted side by side and mix from the contact surface on. Since both are cold, ignition does not take place immediately. It occurs only after a certain prewarming zone [zone (3)  $G' + L'$  in Fig. 145]. The surface  $R' = 0$  is the ignition surface. Between pure gas [ $G' = 1$ , field (1)] and pure air [ $L' = 1$ , field (2)] and the reaction zone (6) are contained the fields (4) (gas + reaction gas,  $G' + R = 1$ ), as well as (5) (air + reaction gas,  $L' + R' = 1$ ). The reaction zone itself does not form here into an extremely thin layer that might be regarded as a surface, but rather it can be extended at will for the following reason: Fresh gas (+ $R$ ) and air (+ $R$ ) enter field (6) by turbulence, *i.e.*, individual ribbons and threads of gas flow around each other here in an irregular manner from fields (4) and (5). Between the individual partial fields of the composition (4) or (5), the diffusion and the reaction take place in a very thin bordering layer; but, since the region that is filled in such an irregular manner by gases from fields (4) and (5) as well as by reaction products is finite in extent, conversion also extends over such a region.

To illustrate further, it is necessary to supply the concentrations of the individual components in the individual fields from place to place.

<sup>1</sup> If the fresh gas contains hydrocarbons in addition to  $\text{CO}$  and  $\text{H}_2$ , the various components will be variously combined by incomplete combustion. The percentage of these various entities is therefore in itself not the characteristic feature for the combustion condition.

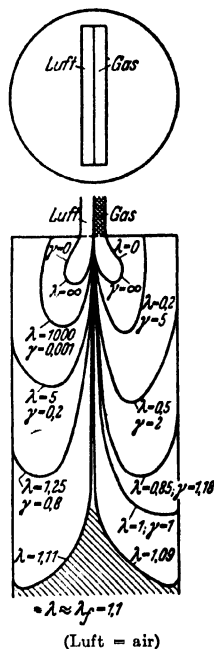


FIG. 146.—Proportions of mixture as gas and air leave a batwing burner and enter a burner space with the terminal condition  $\lambda_f = 1.1$ . ( $\lambda$ , air factor,  $\gamma$ , gas factor. Compare the text.) (From Rummel, p. 208.)



Since it is the mixing process that is of special interest, the analytical values of Rummel are applied to the composition as it would be at each place without conversion having taken place. The simplest factor thus obtained is the "air factor"  $\lambda$ , that is, the ratio between the mass of air

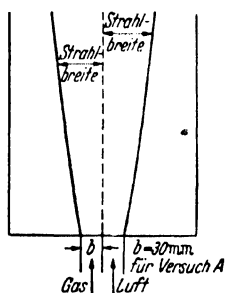


FIG. 147.

(Strahlbreite = width of jet. Für Versuch = for experiment. Luft = air.)  
 (Strahlbegrenzung = boundary of jet  
 Kurven der wirklichen Verbrennung = curves of actual combustion  
 Zeitkurven = time curves)

FIG. 148.—Illustration of the jet in the experiments of Rummel.

FIG. 148.—True jet velocity in m/sec in experiment A.

FIG. 149.—Time duration during which the gases remain in firing in experiment A.

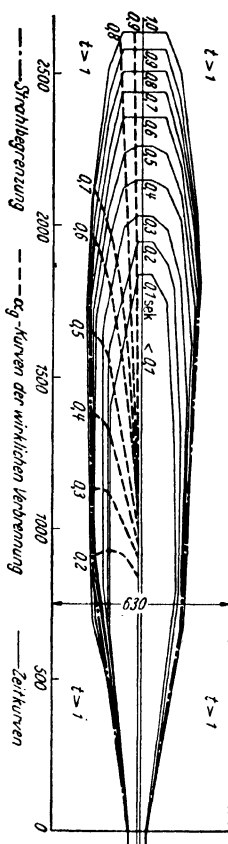


FIG. 148.

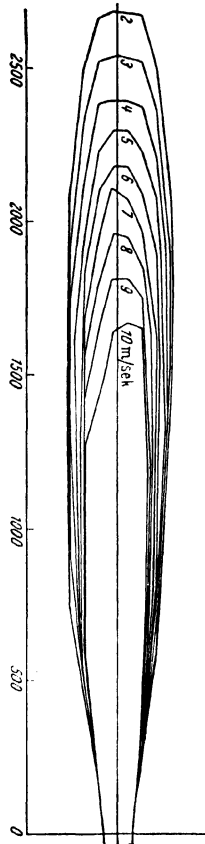


FIG. 149.

actually present and that required for complete combustion. For a stoichiometric gas-air mixture, therefore,  $\lambda = 1$ ; for pure air,  $\lambda = \infty$ ; and, for pure fuel gas,  $\lambda = 0$ .

By analogy, we can also introduce the "gas factor"  $\gamma (= 1/\lambda)$ , which also equals 1 for the stoichiometric mixture, but for pure air = 0 and for

pure gas =  $\infty$ . In this manner, Fig. 146 taken from Rummel illustrates a combustion chamber, assuming that the terminal condition corresponds to the value  $\lambda = 1.1$  (i.e., 10 per cent more air is required than is necessary for complete combustion).

A survey of the flow conditions in the length of an actual burner and of the resulting times of presence of the gases in the burner is given in Figs. 147 to 149 (from Rummel). They require no explanation.

Even though it is impossible to say a priori with certainty that the mixing process is not changed fundamentally by the combustion process,<sup>1</sup> it is at any rate useful to investigate the mixing process separately in

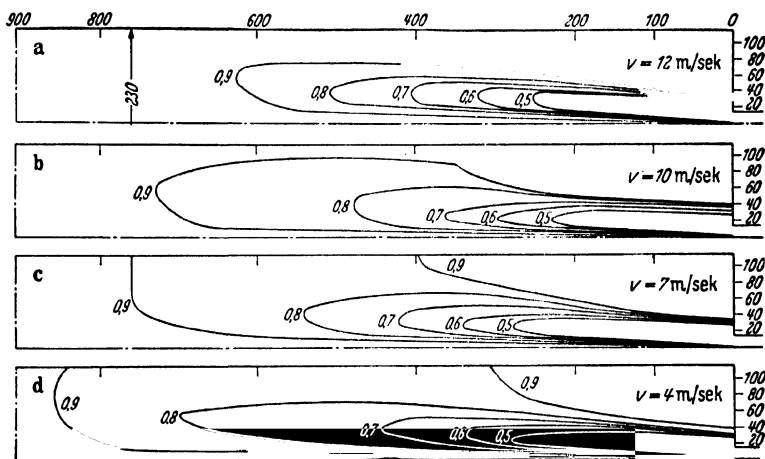


FIG. 150.—Influence of the nozzle velocity  $v$  on the mixing process. Width of slit 14 mm, height of slit 50 mm,  $\lambda$  values. (From K. Rummel, p. 208.)

suitable model experiments. For this purpose, a small experimental length was built in which air and a "gas" consisting of air mixed with 0.5 per cent  $H_2$  was used. The spread of the "gas" could thus easily be determined by means of heat-conductivity measurements made on samples, since, according to this method,  $\frac{1}{100}$  per cent of  $H_2$  in air is still easily determined. Because of the comparisons that are necessary when applying the results obtained from the model length to full-scale operations, we simply refer the reader to Rummel (cited page 210). Of the results thus obtained, we shall give only a small sample. Figure 150 shows a series of experiments in which the load and the resulting velocity of the escaping gases were changed with gas-exit slits of 14 by 50 mm.

<sup>1</sup> Special experiments have shown that the process of mechanical mixing is actually determining for the space and time required for combustion under the conditions of practical operation. Between  $900^\circ$  and  $1300^\circ C$ , an influence of the temperature on the velocity of combustion cannot be proved, as would certainly be the case if the reaction velocity played a role. The latter may therefore be regarded as infinitely great for the conditions of actual practice.

Although a greater jet velocity tends to draw the flame lengthwise, the mixing process is fastest at the greatest jet velocity, because the turbulent energy becomes greater and shortens the mixing path more than it is extended by the greater jet velocity (spatially). This is perhaps the most conclusive proof that turbulent mixing and not diffusion determines

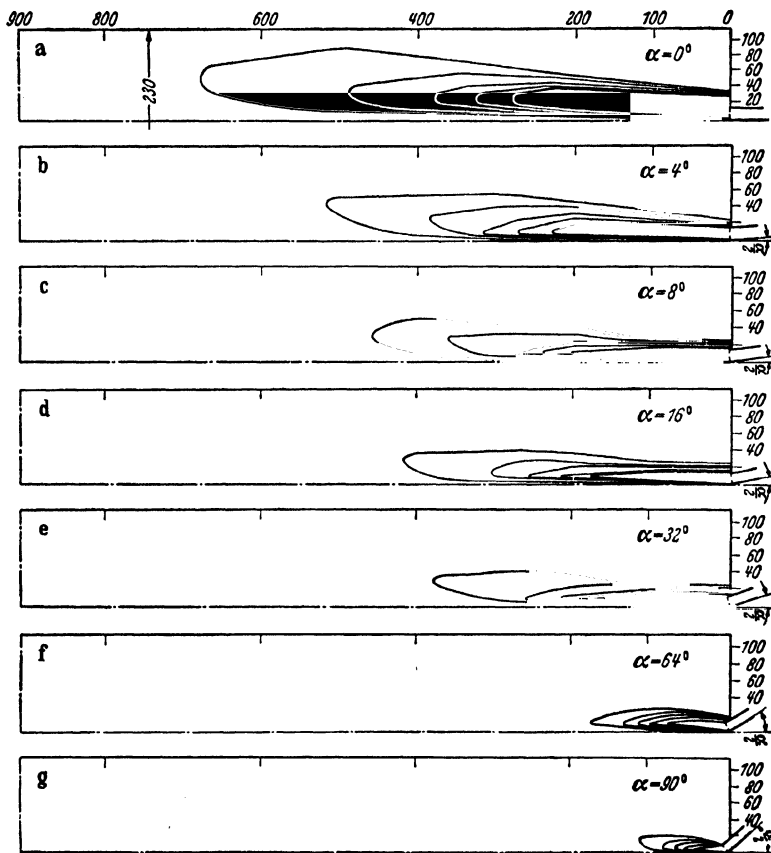


Fig. 151.—Influence of the mutual inclination (angle  $\alpha$ ) of the gas and air jet on the mixing process; values from 0.9 to 0.5, nozzle velocity unchanged, 10 m/sec. Height of slit 50 mm, width 14 mm. (Dimensions in mm.) (From K. Rummel, p. 208.)

the mixing process over large ranges. The inclinations of the air and gas jets have a favorable effect (Fig. 151). An enlargement of the angle at which the jets strike upon one another causes an extraordinary shortening of the mixing space.

Further experiments tested the fact that an application of the results of these model experiments on practical combustion is permissible on the basis of similarity. We refer the reader to the original works.

## CHAPTER VII

### FLAME TEMPERATURES. RADIATION INVESTIGATIONS ON FLAMES

**1. Measuring Flame Temperatures.**—A completely acceptable manner of measuring flame temperatures offers many difficulties. In bomb explosions, the maximum temperature reached can best be determined by pressure measurements (what is obtained is in reality a spatial mean value of the temperature of the mixture; cf. Chap. IV, page 148). From the recorded maximum pressure, the temperature of the gases is obtained if the composition of the substances formed is known (there is probable dissociation at high temperatures), assuming, as may generally be done, that the laws of ideal gases hold. In this manner, bomb explosions are used to determine the specific heats of gases.

Direct measurement of temperature, by means of a thermocouple or a resistance thermometer sometimes used in bomb explosions, yields uncertain results if only because of the inertia of adjustment during the short time of the explosion. Even if we attempt to reduce the inertia of adjustment by the use of very thin wires, other sources of error remain that appear also in the case of temperature measurements of statically burning flames, especially errors by heat conduction and radiation. Especially at high temperatures, radiation becomes noticeable and cannot, like conduction, be eliminated by the use of very thin wires. Hopkinson<sup>1</sup> has shown that, at gas temperatures of 1600° to 1800°C and with the use of wires of only 0.25 mm diameter, a temperature difference of 180° to 200°C can appear between wire and gas as the result of radiation. Nevertheless, it is possible in the case of static flames to arrive at exact temperature measurements by giving the wire inserted into the flame as much energy by means of electrical heating as it gives off by radiation.<sup>2</sup> In practice, this is done by measuring the radiated energy directly (*e.g.*, with a bolometer). Then the radiated energy is graphed as a function of the temperature of the wire, which is likewise measured, when the wire is without current and is then heated to various measured high temperatures by various electrical energies. The electrical energy given the

<sup>1</sup> HOPKINSON, *Proc. Roy. Soc. London*, A, **77**, 387 (1906).

<sup>2</sup> SCHMIDT, H., *Ann. Physik*, **29**, 1027 (1909). KOHN, H., *Ann. Physik*, (4), **44**, 749 (1914).

We assume that the conditions of experiment are so chosen that loss of heat by conduction through the wire is excluded.

wire (or rather the current intensity  $i$  used within a series of experiments as a measure of the energy) is likewise graphed as a function of the temperature of the wire (Fig. 152). At a certain temperature  $T_1$ , the two curves intersect. Here the radiated energy is equal to the electrical energy, and as a result this temperature must be equal to the flame temperature, for we have assumed that the wire gives off energy only by radiation. If this energy is exactly supplied by the electrical energy, however, the wire exchanges no energy with the surrounding flame, and both therefore have the same temperature. Determining the energy given off by the wire can be avoided by proceeding in the following manner:<sup>1</sup> As above, the temperature of the wire in the flame is plotted at various heating-current intensities. The energy emitted by the wire by radiation is obtained (assuming that conduction losses are negligible)

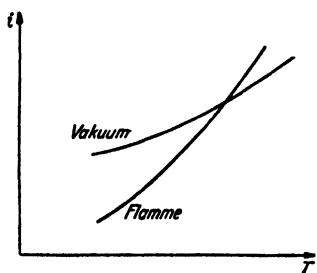


Fig. 152.

by heating the same wire in a vacuum and plotting its temperature as a function of the heating energy (or the heating-current intensity). Under these assumptions, the electrical energy furnished and the energy lost by conduction must obviously be identical. If, therefore, the heating energies of the wire in the vacuum and in the flame are plotted as a function of the temperature of the wire, exactly the same curves must be obtained as in Fig. 152, and their intersec-

tion again yields the true flame temperature. The temperature of the wire itself is most easily measured by an optical pyrometer unless the wire is a thermocouple or a resistance thermometer.

Most of the other methods for determining flame temperatures make use of the properties of radiation. According to Kirchhoff's law, the ratio between emission power and absorption power is constant for all bodies and equal to the emissive power of a black body at the same temperature. If a hot absorbing gas is brought in front of a black body, the radiation of the black body through the gas will appear unchanged if the gas and the black body have the same temperature, for then the hot gas absorbs exactly as much radiation as it again emits. This principle can most easily be applied as a method for temperature measurement in selectively absorbing materials (*e.g.*, Na vapor). If we place cold Na vapor in the radiation path of a black body and observe the radiation in a spectroscope, we shall see a dark absorption line at the *D*-line. If

<sup>1</sup>LOOMIS, A.G., and G. ST. J. PERROT, *Ind. Eng. Chem.*, **20**, 1004 (1928). GRIFFITH, E., and J. H. AWBERY, *Proc. Roy. Soc. London, A*, **123**, 401 (1929). Cf. also LEWIS, B., and G. v. ELBE, *Phil. Mag.*, (7), **20**, 44 (1935); *Chem. Rev.*, **21**, 413 (1937). LEWIS, B., and G. v. ELBE, "Combustion, Flames and Explosion of Gases."

we heat the vapor to exactly the temperature of the black body, the dark absorption line, according to what has been said above, must disappear. If the vapor is heated still further, the *D*-line will stand out as a bright line on the background of the continuous spectrum of the dark body. If, conversely, we are dealing with a hot vapor of unknown temperature, we vary the temperature of the black body. As long as its temperature is lower than that of the gas, the bright emission line of the gas is observed. If the temperature of the black body is higher, the dark absorption line is observed. The temperature of the black body at which the change of line occurs is obviously the temperature of the gas. This method of the change of line was first used by Kurlbaum and Féry.<sup>1</sup> It has been used much since and yields reliable results if applied under the proper conditions (cf. Kohn, H., cited page 219).

Since flame gases are hardly absorbent in the visible portion of the spectrum, absorbing vapors are usually added, *e.g.*, alkali metals, especially sodium. If the vapor has taken on only the temperature of the flame and if the added amount is so small that it does not influence the temperature of the flame, the nature of the added vapor plays no role; nor does anything depend on its concentration or the thickness of the layer applied to the path of radiation, since emissive and absorptive power change equally for these factors. It has been experimentally verified by Kohn (cited page 219) that the density of the illuminating gas is immaterial since it was varied in the ratio 1:2000. It was further demonstrated that the same flame temperature was obtained by the addition of various salts. Errors appear if the temperature in the "colored" gas layer is not constant in the direction of radiation. If the entire gas mass of a Bunsen burner is colored, the outer colder portions will affect the temperature measurement and yield too low a temperature. If only the inner part is colored, a correspondingly higher temperature is found. The application of this method also assumes that we are actually dealing with heat radiation (in contrast to chemiluminescence; cf. page 235).<sup>2</sup> It is not probable that we are dealing with pure heat radiation in the burning zone itself; and, in individual cases at any rate, there is direct evidence for the opposite (see page 235). In practical temperature measurements according to the line-change method, however, it is not the temperature

<sup>1</sup> KURLBAUM, F., *Physik. Z.*, **3**, 332 (1902). KURLBAUM, F., and G. SCHULZE, *Ber. deut. chem. Ges.*, **5**, 428 (1903). FÉRY, *Compt. rend.*, **137**, 909 (1903).

<sup>2</sup> For experimental techniques and a discussion of the method, we refer especially to the following: HENNING, F., and C. TINGWALDT, *Z. Physik*, **48**, 805 (1928). LEWIS, B., and G. v. ELBE, *Phil. Mag.*, (7), **20**, 44 (1935). *Chem. Rev.*, **21**, 421 (1937). JONES, G. W., B. LEWIS, J. B. FRIAUF, and G. ST. J. PERROT, *J. Am. Chem. Sci.*, **53**, 869 (1931). LOOMIS, A. G., and G. ST. J. PERROT, *Ind. Eng. Chem.*, **20**, 1004 (1938). LEWIS, B., and G. v. ELBE, *Engineering*, February, 1935. For a critical discussion, cf. K. F. BONHOEFFER, *Z. Elektrochem.*, **42**, 449 (1936).

in the burning zone that is measured but rather that of the hot gases at a certain distance above the burning surface where no essential reaction takes place and where the conditions for temperature radiation are more likely to prevail. Nevertheless, it is advisable in general to check the method by determining the temperature independently by means of another method, *e.g.*, wire probes (see above) or by working with various colored additions (*e.g.*, Na and Li). Below we give a critical survey of such values by Bonhoeffer.

Instead of using the line-change method, we can also determine emissive and absorptive power of the flame directly and compute the temperature from them. In actual practice, we must employ the ultrared radiation (*e.g.*, CO<sub>2</sub> bands) of the flame (since the radiation and absorption in the visible and the ultraviolet are too weak). If it is a matter of pure temperature radiation, we must obtain the same temperature from the emissive and absorptive power at various wave lengths that coincides with the temperatures obtained by other methods. Examples of this are also contained in the following survey by Bonhoeffer.

Where the line-change method can be used, it is to be recommended because of its simplicity. As a source of light (instead of the black body), a tungsten ribbon light is generally used. Since the emissive power of the tungsten as a function of wave length and temperature is known, all the entities for temperature computation are given, especially if in addition the temperature of the tungsten is measured with a pyrometer.<sup>1</sup> The survey in Table 42 shows that the line-change method, applied with necessary caution, at least yields satisfactory results.

For further measurements of flame temperatures see reference 2.

David and his associates<sup>3</sup> have repeatedly concluded from their experiments that the burned gases still contain considerable quantities of "latent energy" at explosion (in other words, nonthermal energy), and they have made objections in principle to the application of the line-change method for temperature measurements. To be sure, caution is recommended in employing this method for the reasons already mentioned, especially if the method is applied to a burning zone in which a nonthermic radiation can be emitted; and it is well always to test the

<sup>1</sup> For details of measurement and computation, see Lewis and v. Elbe, "Combustion, Flames and Explosions of Gases."

<sup>2</sup> KAVELER, H.H., and B. LEWIS, *Chem. Rev.*, **21**, 421 (1937); v. ELBE, G., and B. LEWIS, *Chem. Rev.*, **21**, 413 (1937).

<sup>3</sup> DAVID, W.T., and DAVIES, *Phil. Mag.*, (7), **9**, 402 (1930). DAVID, W.T., DAVIES, and J. JORDAN, *Phil. Mag.*, **12**, 1034 (1931). DAVID and J. JORDAN, *Phil. Mag.*, **17**, 172 (1934); **18**, 228 (1934); *Nature*, London, **135**, 470 (1935). DAVID, *Phil. Mag.*, (7), **20**, 65 (1935); *Nature*, London, **138**, 930 (1936); *Phil. Mag.*, (7), **21**, 280 (1936). DAVID and S. LEAH, *Phil. Mag.*, **22**, 513 (1936). DAVID, *Nature*, London, **139**, 67, 289 (1937); *Phil. Mag.*, (7) **23**, 251, 345 (1937); *Engineering*, **138**, 475 (1934).

TABLE 42.—OPTICAL TEMPERATURE MEASUREMENTS OF FLAMES (FROM BONHOEFFER)

| Type of flame                               | Method                        | Wave length               | $T^{\circ}$ measured        | $T$ by other methods   | Remarks  |
|---|-------------------------------|---------------------------|-----------------------------|--|--|
| Méker burner (illuminating gas)             | Determining release of energy | 4.39 $\mu$                | 1639°                       | 1640° (pyrometry of a wire probe)                                | With two burners to increase the absorption <sup>1</sup>   |
|   | Determining release of energy | 3.00 $\mu$                | 1670°                       |  |  |
| Méker burner (illuminating gas)             | Kurlbaum and Féry             | D-line (also K, Li, Ti)   | Between 1500° and 1800° abs | Pyrometry of a wire probe + 10° agreement                        | Emphasis on agreement between reverse temperature and flame temperature; not on absolute value of the flame temperature <sup>2</sup> |
| Bunsen flame                                | Kurlbaum and Féry             | D-Line                    | 1981°                       | 1978° (with Li by the same method)                               | Salt coloring over the inner cone <sup>3</sup>   |
| Acetylene-oxygen welding burner             | Kurlbaum and Féry             | Li-Line                   | 2850° abs                   | 2780° (from ultrared radiation 4.39 $\mu$ )                      | Height 30 mm above the burner rim (hot-test place 3100°) <sup>4</sup>  |
| Méker burner (variation) (illuminating gas) | Kurlbaum and Féry             | D-Line                    | 1750°                       | 1770° (pyrometry of a heated wire probe)                         | Variation of the mixture ratio gas: air <sup>5</sup>   |
| Méker burner (illuminating gas)             | Kurlbaum and Féry             | D-line                    | 1730°                       | 1736° (with Li by the same method)                               |  |
|   |                               | D-line                    | 1883°                       | 1877°  | Wire thickness of the probe, 0.5 mm 0.2 mm <sup>6</sup>  |
| Méker burner, hydrogen-air                  | Kurlbaum and Féry             | D-line                    | 2045°                       | 1886° 2047°  |  |
| Carbon monoxide-air                         | Kurlbaum and Féry             | D-line                    | 1955° (1985°)               | 2082°  | Computation without radiation correction <sup>6</sup>  |
| Methane-air                                 | Kurlbaum and Féry             | D-line                    | 1820°                       | 1844°  |  |
| Gasoline engine                             | Determining release of energy | Quartz-permeable ultrared | 2800° abs                   | 2750° abs  | Good agreement only with a definite mixture ratio of gasoline and air <sup>7</sup>   |
| Gasoline engine                             | D-reverse, Kurlbaum and Féry  | D-line                    | 2310°                       | 2373° (ultrared) emission determination. Absorption <sup>8</sup> |  |
| Carbon monoxide-oxygen explosion            | Kurlbaum and Féry             | D-line                    |                             |  | Agreement only in the case of the stoichiometric mixture CO : O <sub>2</sub> <sup>9</sup>  |

<sup>1</sup> SCHMIDT, H., *Ann. Physik*, **29**, 998 (1909).<sup>2</sup> KOHN, H., *Ann. Physik*, **44**, 749 (1914).<sup>3</sup> HENNING, F., and C. TINGWALDT, *Z. Physik*, **48**, 805 (1928).<sup>4</sup> LOOMIS, A.G., and G. ST. J. PERROT, *Ind. Eng. Chem.*, **29**, 1004 (1928).<sup>5</sup> GRIFFITH, E., and J.H. AWBERY, *Proc. Roy. Soc. London, A*, **123**, 401 (1929).<sup>6</sup> JONES, LEWIS, and SEAMAN, according to LEWIS and v. ELBE, *Phil. Mag.*, (7), **20**, 44 (1935).<sup>7</sup> HERSHEY, A.E., *Ind. Eng. Chem.*, **24**, 867 (1932).<sup>8</sup> HERSHEY, A.E., and R.F. PATON, *Phys. Rev.*, **40**, 1053 (1932).<sup>9</sup> DAVID, *Nature*, **135**, 471 (1935). DAVID and JORDAN, *Phil. Mag.*, **18**, 228 (1934).



conditions under which it is to be applied. Nevertheless, the objections by David are in general not valid, and it will be safe to accept the judgment of Lewis and v. Elbe,<sup>1</sup> who reject the idea of a latent energy.<sup>2</sup>

For measurements of gas temperatures, we refer particularly to Hase.<sup>3</sup>

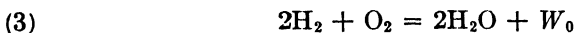
**2. Calculating the Maximum Flame Temperatures.**—The maximum temperature of flames can be computed directly from the expression for the conservation of energy if the heat capacity of the reaction products and the heat of reaction are known. If  $T_0$  is the initial temperature,  $T_e$  the maximum temperature,  $\bar{c}$  the average heat capacity of the reaction products, and  $W_r$  the heat of reaction liberated at  $T_0$ , then obviously the following is valid:

$$(1) \quad \bar{c}(T_e - T_0) = W_r$$

from which, with  $W_r$ ,  $\bar{c}$ , and  $T_0$  known,  $T_e$  would directly follow. For practical calculation, it is necessary to consider the following: Since the heat capacity  $c$  is a function of the temperature, the average specific heat  $\bar{c}$  between  $T_0$  and  $T_e$  is defined by

$$(2) \quad \bar{c} = \frac{\int_{T_0}^{T_e} c \, dT}{T_e - T_0}$$

It is therefore known only if  $T_e$  is known, and  $T_e$  can therefore be determined only by trial.<sup>4</sup> Further,  $W_r$  is the actual heat of reaction, i.e., in a reaction like



where  $W_0$  is the heat of reaction liberated for the formula conversion and  $W_r$  is not identical with  $W_0$ ; for there is no complete conversion in an oxygen-hydrogen explosion since an equilibrium is established and the liberated heat energy is only a portion  $\eta$  of  $W_0$  which corresponds to the actual degree of conversion  $\eta$ . In addition, a part of the water formed dissociates according to



as well as a part of the  $\text{H}_2$  according to



<sup>1</sup> LEWIS, B. and G. v. ELBE, *Engineering*, **139** (Feb. 1935); *Phil. Mag.*, (7), **20**, 44 (1935); also "Combustion."

<sup>2</sup> Recent measurements by H.G. WOLFHARD, *Z. Phys.* **112**, 107 (1939) have shown, as was to be expected, that the energy distributed within the C-C bands does not give the true flame.

<sup>3</sup> HASE, R., *Verfahren und Fehler bei Gastemperaturmessungen*, *Z. Ver. deut. Ing.*, **81**, 571 (1937); with extensive bibliography.

<sup>4</sup> Since  $c$  is not represented by a power expression that can be directly integrated.

and a (smaller) part of the  $O_2$  according to



All three dissociation reactions are endothermic, and the heat of dissociation required by them must be deducted from  $\eta W_0$  if the actual heat of reaction  $W_r$  is to be obtained. It is also necessary to know the flame temperature for computing the equilibriums (3) to (6). Thus it is possible to obtain the end results only by trial.

All the specific heats and equilibrium constants necessary for computation are now available for all cases of practical interest. For specific heats, the values gained from spectroscopic data can be accepted; and, for the computation of the equilibriums, the constants derived from spectroscopic data can likewise be used to a considerable extent. The computation of the equilibriums should follow from Nernst's theorem or one of the approximation formulas derived from it. It is unnecessary to discuss the calculations here if only because the results necessary for all the reactions coming into consideration in combustion processes are tabulated in the literature with sufficient exactness, and a repetition of the computations in individual cases would be unnecessary. In combustion processes, it is normally a matter of C- and H-combinations, and the following appear as reaction products of the combustion: CO, CO<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O, O<sub>2</sub>, and their dissociation products; also atmospheric nitrogen and (with air) NO. Thus, if it is desired to compute the maximum combustion temperature of any carbon-hydrogen-oxygen combination, it is necessary to know only the specific heats of the above combinations and their dissociation products, the equilibrium constants of the individual reactions, and the heat release of the combustion under normal conditions. It is necessary to know the specific heat of the initial substance during a limited temperature interval only if the heat production of the reaction at the initial temperature is not known and must be recomputed from Kirchhoff's principle. If  $W$  is the heat of reaction,  $c_0$  the heat capacity of the initial material, and  $c$  that of the terminal products, then

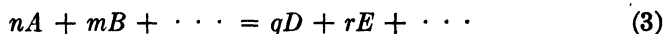
$$\frac{\partial W}{\partial T} = c_0 - c \quad (1)$$

and from it, by integration

$$W^T = W^0 + \int_0^T (c_0 - c) dT \quad (2)$$

if  $W^T$  is the heat of reaction at the temperature  $T$ ,  $W^0$  that at the initial temperature  $T_0$ . In the preceding formulas, we have not yet determined under what conditions  $c$ ,  $W$ , etc., are to be measured. Most applications deal with conversions at constant pressure. Then the heat production at

constant pressure  $W_p$  is taken, and correspondingly the specific heats at constant pressure  $c_p$ , and, in computing the equilibriums, the equilibrium constants  $K_p$ . In the reaction



$K_p$  is defined by

$$\frac{[p_A]^n [p_B]^m \dots}{[p_D]^q [p_E]^r \dots} = K_p \quad (4)$$

where  $p_A$  is the partial pressure of the components  $A$ , etc. In a bomb explosion where the total volume is constant, the reaction, if the entire mixture would burn evenly, would take place at constant volume. Thus, with  $c_v$ ,  $W_v$ , and  $K_c$ , where  $K_c$  is the equilibrium constant written according to the concentrations (= reciprocal mol-volumes) and is therefore derived from  $K_p$ , if the partial pressures are expressed by the concentrations according to the gas equation ( $v_A = \frac{1}{c_A}$ , etc.), the following would result:

$$p_A = c_A RT = [A] RT \quad (5)$$

If the reaction takes place with a change in the mol-number, a power of  $RT$  still remains after this substitution by which  $K_c$  is differentiated from  $K_p$ . As has been mentioned in Chap. IV, page 154, the maximum pressure is thus generally obtained accurately to within several tenths of a per cent (assuming that the entire charge burns at constant volume); although in reality no constant temperature, but rather a considerable drop in temperature from the inside to the outside, prevails in the bomb at the moment of the completion of combustion. For the more exact computation of the terminal condition, discussed in the same place, it is necessary to compute the combustion temperature at constant pressure (not volume) in every elementary layer. Here the compression effected by the expansion of the portion already burned has raised the temperature before the ignition of the layer, and here too the compression effect of the burning remainder of the charge has once more raised the temperature of the previously burned portion.

Numerical values for the specific heats, etc., are found in tabulations,<sup>1</sup> in the compilation of Zeise,<sup>2</sup> and in Justi.<sup>3</sup>

*Example:* Computation of the maximum temperature of a flame of  $\text{CO} + \text{O}_2$  burning at atmospheric pressure. Let the initial temperature of the gases be  $25^\circ\text{C}$ .

<sup>1</sup> For example, Landolt-Börnstein Tables Annuelles.

<sup>2</sup> ZEISE, H., *Z. Elektrochem.*, **39**, 758, 895 (1933); **40**, 662, 885 (1934).

<sup>3</sup> JUSTI, E., "Spezifische Wärme, Enthalpie, Entropie, Dissoziation technischer Gase," Julius Springer, Berlin, 1938.

The heat of reaction is, with complete conversion at 25°C, ~ 68.1 kcal per mol of burned CO. We use Justi's tables for our calculations. According to these tables, the enthalpy difference of carbon dioxide is, at the highest tabulated temperature, namely, 3000°C, ~ 40.3 kcal/mol. Disregarding dissociation, we should expect a flame temperature far over 3000°C; but, since, at 3000°C, likewise according to figures given by Justi, there would have been a dissociation in the neighborhood of 50 per cent according to



and thus only about half the heat of reaction would be liberated, the temperature actually attained would necessarily be correspondingly lower. We shall therefore compute provisionally with  $T = 3000^\circ \text{ abs} = 2727^\circ \text{C}$ . For this temperature, the tables show

$$K_p^I = \frac{p_{\text{CO}} p_{\text{O}_2}^{1/2}}{p_{\text{CO}_2}} = 0.335$$

Since we are assuming atmospheric pressure,  $p_{\text{CO}} + p_{\text{O}_2} + p_{\text{CO}_2} = 1 \text{ atm}$ , and since further  $p_{\text{CO}} = 2p_{\text{O}_2}$ , or  $p_{\text{CO}_2} = 1 - 3p_{\text{O}_2}$ , then

$$\frac{2p_{\text{O}_2}^{3/2}}{1 - 3p_{\text{O}_2}} = 0.335$$

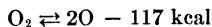
and thus  $p_{\text{O}_2} = 0.1805$ , as can be determined most rapidly by trial. As a result,  $p_{\text{CO}} = 0.361$ ,  $p_{\text{CO}_2} = 0.458 \text{ atm}$ . The degree of conversion  $\eta$ , the ratio of  $\text{CO}_2$  formed to the CO originally present, becomes

$$\eta = \frac{p_{\text{CO}_2}}{p_{\text{CO}_2} + p_{\text{CO}}} = 0.559$$

Thus the effective heat production becomes  $W_r = \eta W_0 = 38.1 \text{ kcal}$ . With the above value of  $\eta$ , 1 mol of CO and  $\frac{1}{2}$  mol of  $\text{O}$  have become

$$0.559 \text{ mol CO}_2 \quad 0.441 \text{ mol CO} \quad \text{and} \quad 0.22 \text{ mol O}_2$$

The sum of the enthalpy differentials of these materials between 25° and 2727°C becomes  $20.24 + 9.85 + 5.16 = 35.25 \text{ kcal}$ . We have still forgotten one correction, however. For 3000° abs, we find the reaction



$$K_p^{II} = \frac{p_{\text{O}}^2}{p_{\text{O}_2}} = 1.4 \cdot 10^{-2}$$

If the partial pressure of oxygen (of atoms + molecules) were held constant at 0.181 atm, a degree of dissociation of the oxygen of ~ 0.12 would result; therefore (only as a preliminary estimate), since 0.22 mols of  $\text{O}_2$  were still present with a dissociation heat of 117 kcal, there would be an amount of energy of ~  $0.22 \cdot 0.12 \cdot 117 \text{ kcal} = 3.1 \text{ kcal}$  to be spent, to the extent of which  $\eta W_0$  would have to be reduced. The assumed temperature of 2727°C was therefore a little too high, and thus we repeat the computation of 2720°C = 2993° abs by introducing the  $\text{O}_2$  dissociation initially.

At 2993° abs (as can be obtained by interpolation, most effectively on graphs by plotting  $\log K_p$  against  $1/T$ , employing logarithmic-hyperbolic coordinate paper)

$$K_p^I = \frac{p_{\text{CO}} \cdot p_{\text{O}_2}^{1/2}}{p_{\text{CO}_2}} = 0.32 \quad K_p^{II} = \frac{p_{\text{O}}^2}{p_{\text{O}_2}} = 1.37 \cdot 10^{-2}$$

$$p_{\text{O}} = 0.117 \sqrt{p_{\text{O}_2}}$$

Further, the following must result:

$$\begin{aligned} p_{\text{CO}} + p_{\text{CO}_2} + p_{\text{O}_2} + p_{\text{O}} &= 1 \text{ atm} & 2p_{\text{O}_2} + p_{\text{O}} &= p_{\text{CO}} \\ p_{\text{CO}} &= 2p_{\text{O}_2} + 0.117 \sqrt{p_{\text{O}_2}} \\ p_{\text{CO}_2} &= 1 - 3p_{\text{O}_2} - 0.234 \sqrt{p_{\text{O}_2}} \end{aligned}$$

Hence

$$\frac{2p_{\text{O}_2}^{3/2} + 0.117p_{\text{O}_2}}{1 - 3p_{\text{O}_2} - 0.234 \sqrt{p_{\text{O}_2}}} = 0.32 = K_p^I$$

$$p_{\text{O}_2} = 0.156 \quad p_{\text{O}} = 0.046 \quad p_{\text{CO}} = 0.358 \quad p_{\text{CO}_2} = 0.440 \text{ atm}$$

The degree of formation of  $\text{CO}_2$  is therefore

$$\eta = \frac{0.44}{0.44 + 0.358} = 0.552$$

and the degree of dissociation of the oxygen is

$$\alpha = \frac{1/2 p_{\text{O}}}{p_{\text{O}_2} + 1/2 p_{\text{O}}} = 0.128$$

The effective heat production becomes

$$W_r = \eta 68.1 - \alpha(1 - \eta)0.5 \cdot 117 = 34.25 \text{ kcal}$$

There are still present (mols)

$$\text{O}_2:0.196 \quad \text{CO}:0.450 \quad \text{CO}_2:0.552 \quad \text{and} \quad \text{O}:0.058$$

The sum of their enthalpy differentials between  $25^\circ$  and  $2720^\circ$  becomes

$$20.20 + 10.14 + 4.64 + 0.78 = 35.76 \text{ kcal}$$

The temperature was thus assumed at too high a figure. We repeat the computation for  $2700^\circ\text{C}$  ( $2973^\circ$  abs) and find

$$\begin{aligned} K_p^I &= 0.295 & K_p^{II} &= 1.20 \cdot 10^{-2} \\ p_{\text{O}_2} &= 0.152 & p_{\text{O}} &= 0.043 & p_{\text{CO}} &= 0.347 & p_{\text{CO}_2} &= 0.458 \\ \eta &= 0.569 & \alpha &= 0.124 \\ W_r &= 38.8 - 3.12 = 35.68 \text{ kcal} \end{aligned}$$

The mol-numbers are

$$\begin{array}{cccc} \text{CO}_2 & \text{CO} & \text{O}_2 & \text{O} \\ 0.569 & 0.431 & 0.188 & 0.053 \end{array}$$

and the sum of the enthalpy differentials for this between  $25^\circ$  and  $2700^\circ$  is

$$20.8 + 9.70 + 4.45 + 0.71 = 35.66 \text{ kcal}$$

is sufficient agreement with  $W_r$ ;  $2700^\circ$  can therefore be regarded as sufficiently exact for the maximum temperature. In other cases, the computation may be carried out in a similar way, except that, with hydrogen present, the dissociation equilibria of the vapor and the hydrogen are to be taken into account, as well as the water-gas equilibrium and the NO equilibrium in air.

It is possible to approximate the entities entering the calculation by power equations and thus to execute the temperature computation directly, without trial.<sup>1</sup>

<sup>1</sup> ZEISE, H., *Feuerungstech.*, **26**, 145, 278 (1938).

Given suitable tables like those of Justi, however, it is likely that the trial method, assuming skillful application, is more convenient.

**3. Spectroscopic Analysis of Flames.**<sup>1</sup>—In flames of oxygen and hydrogen with air, an intense band spectrum in the ultraviolet may always be observed, with the strongest bands at 3064 Å, which belongs to the radical OH (Fig. 153). These bands are observed moreover in all flames of hydrogen containing combinations as well as of moist CO except at very high pressures.<sup>2</sup> Concerning the role probably played by the radical OH in H<sub>2</sub> (and CO) combustion, see Chap. IX. Under special conditions, it is also possible to observe a longer waved spectrum of an O<sub>2</sub>H<sub>2</sub> flame lying in the visible range. Kitagawa<sup>3</sup> had an oxygen flame burn in a hydrogen atmosphere and obtained a spectrum reaching from 5500 to 7000 Å. A number of the bands coincided with bands that can be observed in water vapor at 144°C in an 8 m long absorption tube with a vapor pressure of 4 atm. For that reason, the spectrum was interpreted as a rotation-wave spectrum of the water molecule. Whether this is correct will probably have to be shown by further investigations.

In the near ultrared, water vapor shows a particularly intensive band at 2.7 μ, which also appears in absorption. It is also possible, by the way, to obtain OH bands in absorption; and, in hydrogen-oxygen flames burning under high pressure, the band at 3064 can sometimes show self-reversal.

The fact that the emission spectrum of a certain radical, in this case OH, is observed in combustion is no proof that this radical plays a special role in combustion, but it does suggest determining the role of this radical for the chemical reaction. It has been found that, in the case of the OH-radical, no doubt can exist as to its participation in combustion. Kondratjew<sup>4</sup> (Kondratyeff) has made a special study of the conditions and not only has measured the intensities of OH bands in emission but also has determined the concentration of OH in flames, which he found to be higher than would correspond to the equilibrium (*cf.* Chap. IX). In addition, he noted in attenuated flames an intensity distribution of the individual partial bands that excludes a thermal influence and allows only for chemiluminescence as the causal factor. It is also possible to compute the temperature of flame from the relative intensity of the various rotation lines within a partial band, as Kondratjew has partly done with success. A presupposition for this method, in itself suitable

<sup>1</sup> *Cf.* in this connection BONHOEFFER, K.F., *Z. Elektrochem.*, **42**, 449 (1936).

<sup>2</sup> BONE, W.A., and F.G. LAMONT, *Proc. Roy. Soc. London, A*, **144**, 250 (1934).

<sup>3</sup> KITAGAWA, T., *Proc. Imp. Acad. Tokyo*, **12**, 281 (1936); *Rev. Phys. Chem. Japan*, **10**, 317 (1936).

<sup>4</sup> KONDRATJEW, V., and M. ZISKIN, *Acta Physicochim. URSS*, **5**, 301 (1936); **6**, 307 (1937); **7**, 65 (1937). AYRAMENKO, L., and V. KONDRATJEW, *Acta Physicochim. URSS*, **7**, 567 (1937). KONDRATJEW, V., *Acta Phys. Polon.*, **5**, 65 (1936).

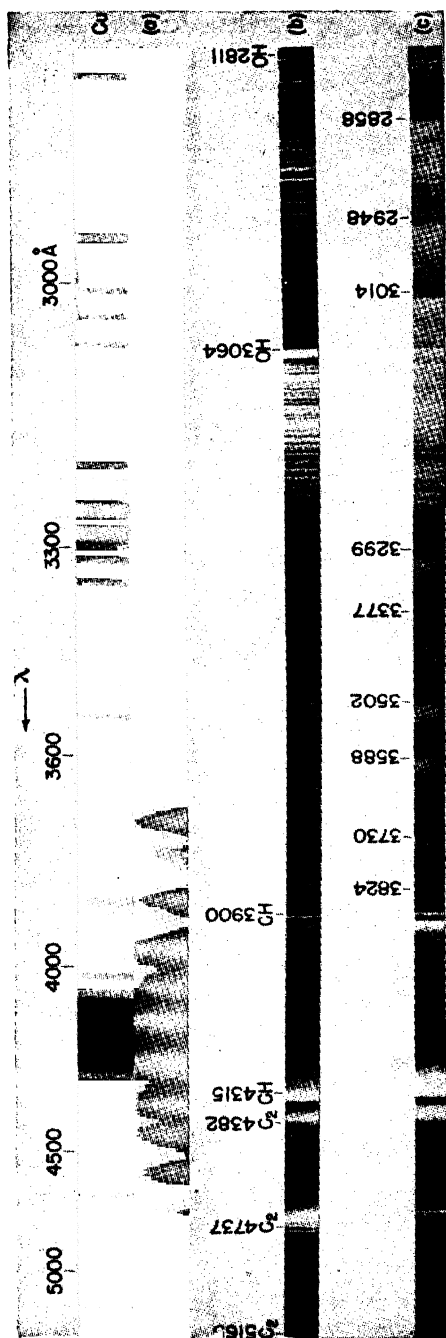


Fig. 153.—Flame spectra. *a*. "Cold flames" of ether. (Cu spectrum for comparison.) *b*. Spectrum of the normal flame with C, CH, and OH bands. *c*. "Vaidya" bands in the ethylene flame in addition to C, CH, and OH bands. (The author is indebted to Dr. R. W. B. Pearse, Imperial College, South Kensington, for reproductions of these spectra.) (From *Emeléeus*.)

for wider application, is, however, that the individual rotation conditions are present in the concentration corresponding to the thermal equilibrium, and this need not necessarily be the case in the burning zone itself.

Carbonic acid in absorption shows a series of bands in the ultrared, of which the band at  $4.84\ \mu$  is the most prominent (Fig. 154). This band is shown by the ultrared emission spectrum of  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . In addition to this emission in the ultrared, we further observe in the carbon monoxide-oxygen flame over a continuous background a system of less well defined bands<sup>1</sup> (Fig. 155) extending from the ultraviolet to the visible. Kondratjew ascribes these to  $\text{CO}_2$ . At low pressure, these bands appear more pronounced on the continuous background.

In flames of hydrocarbons, we can especially observe, in addition to the bands mentioned, the band spectrum of the radical  $\text{C}_2$  (the Swan spectrum) (Fig. 153) particularly in the green, as well as the spectrum of  $\text{CH}$  (Fig. 153); of the latter, two bands at  $4317$  and  $3888\ \text{\AA}$ ; and, of the former, the bands at  $4737$ ,  $5165$ , and  $5635\ \text{\AA}$ .

Although it is known that  $\text{OH}$  takes part in the chemical reaction, the same cannot as yet be said of  $\text{CH}$  and  $\text{CC}$ . Perhaps a quantitative investigation of the radiation emitted by the individual radicals under

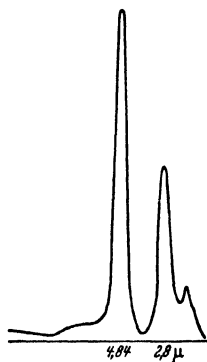


FIG. 154.—Ultrared emission spectrum of  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

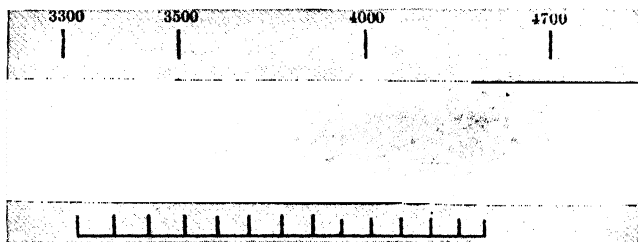


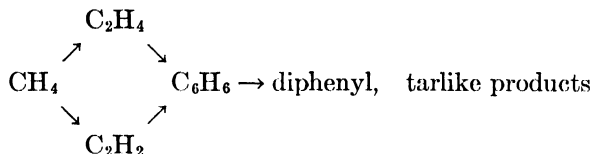
FIG. 155.—Spectrum of burning carbon monoxide.  $\text{CO}_2$  bands ?; one (of six) series is marked at the bottom of the illustration. [From Kondratjew, *Z. Phys.*, vol. 63 (1930).]

various conditions of reaction would lead to further results. It is not improbable that  $\text{CH}$  is produced in the disintegration of hydrocarbon molecules in the flame, *e.g.*, under the attack by  $\text{H}$ -atoms and  $\text{OH}$ -radicals. It is actually possible to observe the  $\text{CH}$  spectrum in "cold flames" of

<sup>1</sup> FOWLER, A., and WESTON, *Proc. Roy. Soc. London*, A, **109**, 176, 523 (1925). KONDRATJEW, V., *Z. Physik*, **63**, 322 (1930). FOWLER, A., and GAYDON, *Proc. Roy. Soc. London*, A, **142**, 362 (1933).



hydrocarbons with hydrogen<sup>1</sup> or oxygen<sup>2</sup> atoms, in both cases in addition to the CC spectrum and the OH spectrum in the case of oxygen atoms. It is conceivable that CC-radicals appear if a molecule with at least two C-atoms is disintegrated to the extent that CC just remains. This is, however, at least not the only way in which CC is formed in the flame, for methane<sup>3</sup> and, somewhat weaker, methanol also show the CC spectrum.<sup>4</sup> It is likely therefore that a polymerization process was also occurring in the formation of CC. According to Bonhoeffer, CC commonly appears under conditions in the flame that suggest that it is the first sign of the process leading to the formation of soot. With considerable air, the inner cone of the Bunsen flame looks bluish (CH bands); whereas, with insufficient air, it appears green (Swan bands, C<sub>2</sub>). Carbon-poor and hydrogen-containing combinations yield a much weaker CC spectrum than carbon-rich combinations like benzol and acetylene. Under conditions at which soot begins to form, the Swan bands (*e.g.*, in benzol and gas oil) appear intensive and apparently continuously broadened (because of the small applied dispersion and probable excess radiation, this cannot be stated with absolute certainty),<sup>5</sup> and this can be interpreted as the incipient further polymerization of the CC-molecules in soot particles. The fact that CC bands also occur in methane does not exclude polymerization processes of the hydrocarbons (or portions derived from them) as a primary process, *e.g.*, in methane (as one of a series of conceivable processes),



with progressing H<sub>2</sub> cleavage. If the formation of soot comes about in such a way and not by polymerization of atomic or molecular C, it would be quite understandable that the more highly molecular combinations are especially suited for that formation. To be sure, polymerizations can also appear under the influence of oxygen, and the polymerization products need not necessarily be hydrocarbons. Bonhoeffer (cited page 229) specifically points out that up to the present there is no reason for assuming that the chief conversion in the combustion of hydrocarbons need necessarily go beyond the radicals C<sub>2</sub> and CH.

<sup>1</sup> BONHOEFFER, K.F., and P. HARTECK, *Z. physik. Chem.*, Sec. A, **139**, 64 (1928).

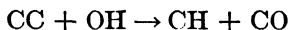
<sup>2</sup> HARTECK, P., and U. KOPSCH, *Z. physik. Chem.*, Sec. B, **12**, 327 (1931).

<sup>3</sup> LAUER, *Z. Physik*, **83**, 179 (1933).

<sup>4</sup> GUÉNAULT, *Safety in Mines Research Board Paper 13; Ann. Rept.*, 1934, p. 66.

<sup>5</sup> ERICHSEN, C., *Ver. deut. Ing. Forsch.*, 1936, p. 377. Cf. also BONHOEFFER, K.F., quoted p. 229.

As a result, it cannot be said with certainty whether the appearance of the CC bands in fuel-rich mixtures and their recession in air-rich flames derives from the fact that there is a considerable formation of CC in one case and not in the other case, or from the fact that  $C_2$  forms in all cases but reacts rapidly with other combinations in air-rich flames, e.g., with OH according to



which would explain the change of the color of the Bunsen cone from green to blue.<sup>1</sup>

In ordinary flames of hydrocarbons, it is often possible to detect in the near ultraviolet a further, somewhat diffuse band spectrum. It can, for example, be seen on a photograph by Emeléus<sup>2</sup> of an ordinary ether flame burning in air. We are interested in the bands approximately between 3300 and 3800 Å, shading off to the red. Under certain circumstances, it is possible to intensify these bands considerably, showing that the system of bands extends from about 2500 to 4100 Å. Vaidya,<sup>3</sup> who first recognized these bands and made a special study of them, could obtain them most intensively in an ethylene flame (Fig. 153). They also appear markedly in photographs taken by Neumann in connection with Diesel combustion (Erichsen, cited page 232, Beck<sup>4</sup>). The Vaidya bands have also been obtained in methane flames [of  $CH_4 + 2.3(O_2 + 2.2N_2)$ ].\* In combustion in air, spectra of nitrogen combination (CN, NO) can appear under certain circumstances, but they need not necessarily have anything to do with the actual course of combustion. In flames of combinations containing nitrogen, like pyridine, aniline, etc., the CN and NO bands can be very intensive (Vaidya). The source of the system of bands observed and analyzed by Vaidya is not known precisely at present. It is reasonable to assume that it is an unknown radical; and, since the simplest radicals CC, CH, and OH do not come into consideration, a conceivable simple radical would be HCO, which should be assumed to be an intermediate product in the reaction of H-atoms with carbon monoxide.<sup>5</sup> HCO is similar to NO in mass and equal to it in the

<sup>1</sup> BONHOEFFER, K.F., and F. HABER, *Z. physik. Chem.*, **137**, 263 (1928).

<sup>2</sup> EMELEUS, H.J., *J. Chem. Soc.*, 1926, p. 2948.

<sup>3</sup> VAIDYA, W.M., *Proc. Roy. Soc. London, A*, **147**, 513 (1934); *Proc. Indian Acad. Sci.*, **2**, 352 (1935) and later works.

<sup>4</sup> BECK, G., Dissertation T.-H. Hannover, *Ver. deut. Ing. Forsch.*, 1936, p. 377.

\* BELL, J., *Proc. Roy. Soc. London, A*, **158**, 429 (1937). We refer to this work especially because of the many photographs of methane explosions and stationary flames under the most varied conditions, including initial pressures up to 100 atm and methanol and formaldehyde flames. The photographs show characteristic variations of the intensities under varying experimental conditions.

<sup>5</sup> FRANKENBERGER, W., *Z. Elektrochem.*, **36**, 757 (1930). HARTECK, P., and W. GROTH, *Z. Elektrochem.*, **44**, 621 (1938).

number of electrons. Molecules with the same number of electrons, of which CO and N<sub>2</sub> are the best known examples, often show a great similarity in their physical behavior. Vaidya has found that there is a formula very much like that of the NO system of bands for the angular system of the bands he analyzed. This fact has induced him to assume HCO as the source of his bands. Even though this is by no means conclusive, it is at least reasonable to regard HCO as the band source for the time being.

In addition to normal combustion, there is in the case of most hydrocarbons a slower combustion in "cold flames." If mixtures of the vapors of organic compounds (paraffins, olefins, naphthenes, aldehydes, alcohols, ether) are conducted into mixtures with air or oxygen through a tube that is heated to temperatures of  $\sim 300^\circ$  to  $400^\circ\text{C}$ ,<sup>1</sup> a pale blue luminescence appears at lower temperatures and a "cold flame" at higher temperatures, which again disappears at higher temperatures still. The cold flame moves at a velocity of  $\sim 10$  to  $20$  cm/sec toward the gas, and the gas is heated by about  $100^\circ$  to  $200^\circ$ , although complete combustion does not take place. On the contrary, great quantities of aldehyde, especially formaldehyde, are found in addition to water and carbon monoxide. In the cold flame, we are dealing with a conversion that has all the characteristics of an explosion, probably a chain explosion, and in which the moderate heating is only a secondary phenomenon. Peculiarly enough, however, the conversion ceases with the above-named products, even though a true explosion can occur from the cold flame under certain conditions.<sup>2</sup> Emeléus<sup>3</sup> has studied the spectrum of the cold flame, first of ether, then of other organic compounds, of acetaldehyde, propionaldehyde, and hexane. The spectrum is the same in all cases. Figure 153 shows the spectrum of the cold flame of ether, which is completely different from that of normal ether combustion. It is also not identical with the Vaidya bands. Its most intensive portion is at essentially longer wave lengths, between about 3600 and 4500 Å. Toward the short-wave side, it extends, with considerably less intensity, to about 2500 Å. This spectrum may be ascribed to formaldehyde, as Kondratjew<sup>4</sup> first concluded from a comparison with the absorption spectrum of formaldehyde investigated by Schou and Henri,<sup>5</sup> and as Ubbelohde<sup>6</sup> later showed by means of a comparison with its fluorescent spectrum.<sup>7</sup>

<sup>1</sup> Luminescence and cold flames already appear partly at essentially lower temperatures, in ethyl ether under  $200^\circ\text{C}$ .

<sup>2</sup> Bibliography and a more thorough discussion will be found in Chap. XI.

<sup>3</sup> EMELÉUS, H.J., *J. Chem. Soc.*, 1926, p. 2948; 1929, p. 1733.

<sup>4</sup> KONDRATJEW, V., *Z. Physik*, **63**, 322 (1930).

<sup>5</sup> SCHOU, S.A., *Compt. rend.*, **186**, 690 (1928). HENRI, V., and S.A. SCHOU, *Z. Physik*, **49**, 774 (1928).

<sup>6</sup> UBBELOHDE, A.R., *Proc. Roy. Soc. London, A*, **152**, 354, 378 (1935).

<sup>7</sup> GRADSTEIN, S., *Z. physik. Chem.*, Sec. B, **22**, 384 (1933).

Certainly this is a case of chemiluminescence, for at the low temperatures of the cold flames no thermal radiation of significant intensity could be emitted in the blue and the ultraviolet. Recently the  $\text{H}_2\text{CO}$  spectrum has also been observed in methanol flames but not in those of methane.<sup>1</sup>

The spectra of the ordinary carbon disulphide flame have also been studied by Emeléus, as well as the cold flame of carbon disulphide. The longer wave portion of the spectrum reaching into the visible, between 4500 and 3400 Å, is identical in both cases. In addition, there is still, in the case of the cold flame, a spectrum between 3100 and 2500 Å reaching into the shorter wave ultraviolet. According to Kondratjew (cited page 234), the first is the spectrum of the  $\text{S}_2$ -molecule, the latter that of the  $\text{SO}$ .

A chemiluminescent radiation of quite exceptional intensity is furnished by explosions of  $\text{CS}_2\text{NO}$  or  $\text{N}_2\text{O}$  mixtures.<sup>2</sup> In this case, too, the  $\text{S}_2$ -molecule seems to be in the main responsible for the light emitted (cf. page 239).

**4. Thermal Radiation and Chemiluminescence.**<sup>3</sup>—The question of whether the radiation emitted from a flame is of thermal origin or a luminescent radiation is of general interest and is important for several reasons. We speak of thermal radiation if intensity and distribution of energy (to the various wave lengths) depend only on the nature of the gas mixture and on its temperature. Since, as has already been mentioned on page 220, according to Kirchhoff's law, the quotient of the emission by the absorption at a given wave length is constant and equal to the emission of the black body, it is possible to compute the emission from the measured absorption as well as from the emission of the black body given by Planck's law of radiation. In the last analysis, all temperature measurements going back to radiation measurements depend on this. A body cannot radiate less than its temperature radiation, but it can under certain circumstances radiate more. In this case, insofar as radiation induced by an incidental outside radiation is excluded, we are dealing with chemiluminescence, the intensity of which is therefore not a pure temperature function for a given material. The energy of the radiation thus emitted must be supplied from a different source than that of the thermal energy, and the only source available in the case of chemiluminescence, in which we are interested here, is the energy of chemical reaction. Thus the energy liberated in a definite step of the reaction must be used to incite radiation before it is distributed by impacts to the extent corresponding to the average thermal energy distribution. Con-

<sup>1</sup> GUÉNAULT, *Safety in Mines Research Board*, Vol. 16, *Ann. Rept.*, 1937.

<sup>2</sup> VAN LIEMPT, J.A.M., and J.A. DE VRIEND, *Rec. trav. chim.*, **52**, 160, 549, 862 (1933). For the spectrum of the  $\text{CS}_2$  flame, see A. FOWLER, and W.M. VAIDYA, *Proc. Roy. Soc. London, A*, **132**, 310 (1931).

<sup>3</sup> Cf. BONHOEFFER, K.F. (quoted p. 229).

versely, we can conclude from the wave length of the observed chemiluminescent radiation that a partial reaction must take place with a heat production that is at least equal to the  $h\nu$  of this radiation. The following cases of pronounced chemiluminescence deserve mention: the phosphorus vapor flame<sup>1</sup> and the reaction luminosity in highly attenuated flames of alkali metals and halogenes.<sup>2</sup>

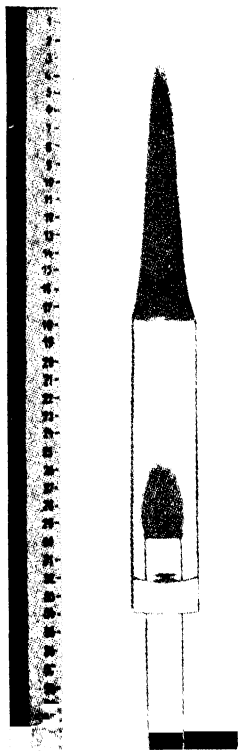


FIG. 156.—Split flame.  
(From Haber and Richardt.)

Haber<sup>3</sup> and Richardt studied the composition of the gases that are formed in the inner cone of the Bunsen burner after penetration of the burning zone in the following manner (Fig. 156). By means of the "flame-splitting tube" described by Teclu<sup>4</sup> and Smithells and Ingle,<sup>5</sup> the combustion in the inner and outer cone of the Bunsen burner was split. A glass tube was affixed airtight to the tube of the burner, preventing the entrance of secondary air into the flame. Thus, at the mouth of the burner itself, only the combustion in the inner cone could take place undisturbed by possible secondary air, and further combustion could take place only at the mouth of the second tube. Haber and Richardt could take gas analyses from the "intermediate gas" by means of a cooled pipette of platinum, and they determined that the composition of the gas there corresponded to the water equilibrium reached in the burning zone. This means, however, that, once the burning surface is penetrated, chemical equilibrium is reached. If no chemical reaction takes place, there can be no chemiluminescence.

For the burning zone of the inner cone itself, this is not true. Even though quantitative measurements are as yet lacking, it is not unlikely

<sup>1</sup> CENTNERSZWER and PETRIKALN, *Z. physik. Chem.*, **80**, 235 (1912). PETRIKALN, *Z. Physik*, **22**, 119 (1924). EMELÉUS, H.J., *J. Chem. Soc.*, **125**, 2491 (1924). RUMPF, K., *Z. physik. Chem.*, Sec. B, **38**, 469 (1938).

<sup>2</sup> HABER, F., and K. ZISCH, *Z. Physik*, **9**, 302 (1922). BEUTLER, H., and M. POLANYI, *Naturwissenschaften*, **13**, 711 (1925). *Z. physik. Chem.*, Sec. B, **1**, 3 (1928). BOGDANDY, ST. V., and POLANYI, *Z. physik. Chem.*, Sec. B, **1**, 21 (1928). POLANYI and G. SCHAY, *Z. physik. Chem.*, Sec. B, **1**, 30 (1928). OOTUKA, H., and G. SCHAY, *Z. physik. Chem.*, Sec. B, **1**, 62, 68 (1928).

<sup>3</sup> HABER, F., and F. RICHARDT, *Z. angew. Chem.*, **38**, 5 (1930).

<sup>4</sup> TECLU, *J. prakt. Chem.*, **44**, 246 (1891).

<sup>5</sup> SMITHELLS and INGLE, *J. Chem. Soc.*, **61**, 204 (1892).

that a part of the radiation emitted there is luminescent radiation.<sup>1</sup> In photographs of the split flame by Haber, we can see that another luminous zone, the "aureole" (halo), appears at the inner cone toward the top. Without doubt, the temperature here is still higher than at a greater distance from the burning surface, but it is difficult to say whether the temperature is the only cause of the luminescence. Other chemical changes do not take place in the aureole; on the contrary, water equilibrium has set in. Haber and Richardt have made special experiments in this direction without arriving at a completely convincing result. The inner cone of the Bunsen flame emits OH, CH, and CC bands; the aureole and the outer cone emit only OH bands with continuous background. If it were not possible to interpret this radiation as pure temperature luminescence, it might be suggested that free radicals from the burning zone are still present in a higher concentration than corresponds to the equilibrium, and that these radicals supply radiation energy by their recombining without causing analytically demonstrable differences in concentration.

In general, however, it appears that it is necessary to consider essentially thermal radiation in the outer cone of the Bunsen burner and to conclude that all optical temperature measurements determined there are valid. It is also necessary, of course, to consider the possibility of disturbances in the not purely thermal radiation. As has already been pointed out elsewhere (page 143), the equalization between translation energy and vibration energy does not proceed immediately at each impact but occasionally demands a larger number of gas-kinetic impacts, up to  $10^5$ . It should not be surprising, therefore, if equilibrium is occasionally not established.<sup>2</sup>

Kondratjew's experiments<sup>3</sup> clearly established the fact that radiation in CO combustion under low pressures is luminescent radiation. The radiation is extinguished by the addition of foreign gas and an increase in pressure in exactly the same manner as in fluorescence. In addition, Kondratjew computes from the absolute intensity of the radiation that, in thermal equilibrium, the number of the stimulated CO<sub>2</sub>-molecules that radiate is smaller by  $10^{18}$  than would have to be assumed from the intensity of the observed rays. Therefore, according to Kondratjew, a

<sup>1</sup> An experiment by H.G. Wolfhard [*Z. Physik*, **112**, 107 (1939)], to measure intensity distribution within the Swan bands shows that it is a matter of luminescent radiation (the computed temperatures are much too high).

<sup>2</sup> KNESER, H., *Ann. Physik*, **11**, 761, 777 (1931). EUCKEN, A., and R. BECKER, *Z. Physik. Chem.*, Sec. B, **20**, 467 (1933) and elsewhere.

<sup>3</sup> KONDRATJEW, V., *Acta Physicochim.*, URSS, **2**, 126 (1935). KONDRATJEW, H., and V. KONDRATJEW, *Acta Physicochim. URSS*, **4**, 547 (1936); **6**, 625, 748 (1937). KONDRATJEW, V., *Acta Phys. Polon.*, **5**, 65 (1936).

large portion of the radiation, not only in the cold flame but also in the normal CO flame, is of nonthermal origin. This is in agreement with many other observations in CO explosions. In carbon monoxide explosions, the heat losses are considerably decreased if a little water vapor or  $H_2$  is added to the dry mixture. On the one hand, this could be caused by the fact that added water vapor extinguishes a luminescent radiation; but, on the other hand, it might be connected with the change of the reaction mechanism in the presence of  $H_2O$  (cf. in this connection Chap. IX).<sup>1</sup>

According to Bone, Newitt, and Townend (cf. Bone, "Flame"), remarkable relations result if the cooling losses in bomb explosions after reaching the maximum pressure for various time intervals are expressed as powers of  $T$ . For example, the following exponents result for the first and second half second after reaching maximum pressure:

TABLE 43.—AVERAGE COOLING VELOCITY AS A POWER OF  $T$  IN THE FIRST AND SECOND HALF SECOND AFTER REACHING THE MAXIMUM PRESSURE IN BOMB EXPLOSIONS (FROM BONE, NEWITT, AND TOWNEND)

| Initial pressure, atm  | 10    |        | 50    |        | 100   |        | 150   |        |
|--|-------|--------|-------|--------|-------|--------|-------|--------|
| Time interval first or second half sec after reaching of $p_m$ ..... | First | Second | First | Second | First | Second | First | Second |
| $2H_2 + O_2 + 4N_2$ .....  | 1.9   | 1.9    | 1.8   | 1.8    | 1.9   | 1.9    | 1.8   | 1.8    |
| $2CO + O_2 + 4CO$ .....  | 2.0   | 2.0    | 3.0   | 2.8    | 3.4   | 2.8    | 4.0   | 2.6    |

The rapid rise of the power exponents for CO explosions with the pressure, especially for the first half second, shows that here too radiation losses make themselves especially strongly felt.

David<sup>2</sup> showed, as could be expected, that in gas explosions by far the greater part of the radiation is emitted only after the maximum pressure has been attained.

For the radiation properties of combustion gases, see Schack<sup>3</sup> and

<sup>1</sup> WOHL, K., and M. MAGAT, *Z. physik. Chem.*, Sec. B, **19**, 117 (1932). WOHL, K., and G. v. ELBE, *Z. physik. Chem.*, Sec. B, **5**, 441 (1929). GARNER, W.E., *Ind. Eng. Chem.*, **20**, 1008 (1928). GARNER, W.E., and C.H. JOHNSON, *J. Chem. Soc.*, 1928, p. 280. GARNER, W.E., and F. ROFFEY, *J. Chem. Soc.*, 1929, p. 1123. GARNER, W.E., and TAWADA, *Trans. Faraday Soc.*, **26**, 36 (1930). HALL and TAWADA, *Trans. Faraday Soc.*, **26**, 600 (1930).

<sup>2</sup> DAVID, W.T., and R.M. PARKINSON, *Phil. Mag.*, (7), **15**, 177 (1933).

<sup>3</sup> SCHACK, A., Der Wärmeübergang in technischen Feuerungen unter dem Einfluss der Eigenstrahlung der Gase, *Sonderreihe Mitt. Wärmetelle Düsseldorf*, No. 55, 1923. Die Strahlung leuchtender Flammen, *Ber. Stahlw.- Aussch. Ver. deut. Eisenhüttenl.*, No. 113, 1926.

Eckert.<sup>1</sup> According to them, under engine conditions, about 15 to 25 per cent of the heat transition is conditioned by gas radiation.

We have already seen that  $\text{CS}_2$  with  $\text{NO}$  or  $\text{N}_2\text{O}$  are examples of chemiluminescence with an extraordinary light intensity. The intensity is so great in these cases that dropped pellets can be used for flashes. Light intensities up to 83 lumens/watt were measured (van Liempt and de Vriend; cf. page 235). Since this intensity is reached by a dark body only at  $5000^\circ$ , it is clear at the outset that we are dealing with a case of luminescence. Complete conversion of the energy into "green" radiation would amount to 680 lumens/watt, which means that over 10 per cent of the entire energy is obtained as radiation in the visible field. This would certainly be increased at higher pressures; for the intensity of the light increases at a greater rate than the pressure, and at pressures under 250 mm Hg it is proportional to the square of the pressure.

**5. Radiation and Temperature in the Engine.**—Combustion in the engine shows no special spectroscopic variations from combustion in the Bunsen burner. Rassweiler and Withrow<sup>2</sup> studied combustion in the Otto engine through a quartz window. By means of a pane rotating synchronously with the engine, it was possible to separate the light of the flame front from that of the after-glowing burned gases. The spectrum of the flame front corresponded to that of the inner cone of the Bunsen flame.  $\text{C}_2$ ,  $\text{CH}$ , and  $\text{OH}$  bands appeared, since it is the same process. In the after-glow, only  $\text{OH}$  bands and a continuous background in the visible range [ $\text{CO}_2(?)$ ] are noted. The after-glow processes are comparable with those in the aureole in the split Bunsen burner (page 236). In the outer cone of the Bunsen burner, essentially the same is observed, but here the comparison is not complete, since fresh air is added. In knocking combustion, differences in the intensities are noted; and, in the knocking zone, the  $\text{C}_2$  and  $\text{CH}$  bands appear weakened. As a probable explanation, we might assume that this is a result of the pre-reaction that has taken place in the unburned parts in knocking combustion.

Spectroscopic investigation of luminescence in the Diesel engine shows<sup>3</sup> that we are dealing mainly with the temperature radiation of luminous carbon particles that can also be used for temperature measurements. We shall treat the absorption spectra observable in the oxidation of organic compounds in another place (Chap. XI).

Complete and exact data for computing maximum temperatures in

<sup>1</sup> ECKERT, E., Messung der Gesamtstrahlung von Wasserdampf und Kohlensäure in Mischung mit nichtstahlendern Gasen bei Temperaturen bis zu  $1300^\circ\text{C}$ , *Ver. deut. Ing. Forsch.*, 387, 1937.

<sup>2</sup> RASSWEILER, G.M., and C.L. WITHROW, *Ind. Eng. Chem.*, **24**, 328 (1932). WITHROW, I.C., and G.M. RASSWEILER, *Ind. Eng. Chem.*, **25**, 923, 1359 (1933).

<sup>3</sup> ERICHSEN, C., *Ver. deut. Ing. Forsch.*, 377, 1936. NEUMANN, K., 1939.



the engine are now available<sup>1</sup> (cf. page 224). On the other hand, the factor of heat conduction, which helps to determine the temperature actually reached, is difficult to determine because of the great role played by turbulence.<sup>2</sup> Many attempts have been made to measure the temperature in the engine directly. Since the use of thermoelements and the like is excluded—except for determining the average temperature during the entire work cycle—it is necessary to depend on optical methods. According to Hershey,<sup>3</sup> practically only the line-change method should be considered. It has already been emphasized that caution is recommended in using this method or any other optical method and that its application is dubious especially in the burning zone itself in case conditions exist for a direct transfer of stimulus energy. According to Hershey, applying this method is not questionable, and the results support this view insofar as the temperatures measured are always more or less considerably under those computed, whereas, in direct transfer of stimulus energy, the temperatures to be measured were too high. In comparing measured and computed temperatures in the engine, the appearance of a temperature gradient in explosions in closed chambers should be taken into account (cf. page 148 and Chap. XII). This can cause temperature differences of hundreds of degrees within the burned gases. In the results of temperature measurements in the engine, it is noteworthy that, even after all corrections have been made, the temperatures measured are about 165° lower than those computed. The only possible explanation for this remaining difference is the cooling of the gases during combustion, which is of course much greater than would be computed for conduction

<sup>1</sup> KÜHL, *Ver. deut. Ing. Forsch.*, 373, 1935. JUSTI, E., quoted p. 226.

<sup>2</sup> There are several recent findings (e.g., by Broeze, Driel, and Peletier) to show that the "temperature" in the engine (computed from the pressure) is higher than that obtained by means of thermodynamic data. This is entirely possible if the stimulus of the inner degrees of freedom of the molecules (cf. p. 142) does not take place rapidly enough; but we should like to raise objections to experiments by Lewis and v. Elbe [*J. Chem. Phys.*, 7, 197 (1939)] that were intended to show this. They enclosed gases in flexible tubes and suddenly compressed them (duration  $\sim 10^{-2}$  sec). The rise in pressure noted in the case of multiatomic gases was higher than that computed adiabatically (2 to 5 per cent). If the effect were real, it should also express itself in sound vibrations of corresponding frequency ( $10^2$ ). But these are normal sound frequencies in which the normal  $\kappa$  values are observed; sound dispersion appears only at considerably higher frequencies. We should therefore prefer to assume for the time being that a different explanation of the facts established by Lewis and v. Elbe will suggest itself (compression of finite, great amplitudes, Hugoniot equation; cf. Chap. V, p. 166).

<sup>3</sup> HERSHEY, A.E., *Chem. Rev.*, 21, 431 (1937), with extensive bibliography. Also *Trans. ASME*, 58, 195 (1936). GRIFFITHS and AWBERRY, *Proc. Roy. Soc. London A*, 123, 401 (1929). RASSWEILER and WITHROW, *SAE J.*, 36, 125 (1935). Cf. also BISAND, L., *Deutsche Kraftfahrt-Forschung*, No. 4, 1938, p. 27. *Z. Ver. deut. Ing.*, 81, 805 (1937). BREVOORT, M.J., *Rev. Sci. Instruments*, 7, 342 (1936).

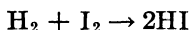
in static gases. Insofar as this is reliable, it might serve to estimate the loss of heat during combustion, which is otherwise very difficult to establish. In applying the line-change method, it must further be taken into account that, since the entire gas is colored, a distorted temperature is determined because the colder layers near the wall (or the window) enter into the calculation.

## CHAPTER VIII

### KINETICS OF COMBUSTION AND EXPLOSION PROCESSES

An intimate knowledge of combustion and explosion processes presupposes a treatment of the kinetics of individual reactions. Since we do not wish to presuppose a knowledge of the general laws of reaction kinetics, a few preliminary remarks in that direction will be made at this point.

**1. Fundamentals of Chemical Kinetics.**<sup>1</sup>—If iodine vapor reacts with hydrogen gas to form hydrogen iodide,

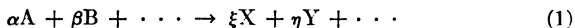


we observe that the velocity of the process, *i.e.*, the increase in the HI concentration with time is given by

$$w = \frac{d[\text{HI}]}{dt} = k[\text{H}_2][\text{I}_2]$$

where the bracketed symbol of a substance gives its concentration. The velocity of the formation of hydrogen iodide is thus proportional to the product of the concentrations of the initial materials. This is the law of the mass action in reaction kinetics.

If a general reaction takes place between the initial components A, B, . . . forming the terminal products X, Y, etc., according to the equation of chemical gross conversion



the velocity of the conversion from left to right [provided that (1) is really determining for the mechanism of conversion<sup>2</sup>] becomes, according to the equation of the law of mass action

$$w = -\frac{d[\text{A}]}{dt} = -\frac{\beta}{\alpha} \frac{d[\text{B}]}{dt} = \dots = +\frac{\xi}{\alpha} \frac{d[\text{X}]}{dt} = k[\text{A}]^\alpha [\text{B}]^\beta \dots \quad (2)$$

in which A is the concentration of the components A, B that of B, etc.  $k$  should probably be designated as "velocity coefficient" (it is commonly called "velocity constant," although it depends at least on the temperature).  $w$ , the reaction velocity, can be thought of as computed from  $t$ , the decrease in concentration of one of the initial products, or from the increase of the concentration of one of the end products.

<sup>1</sup> For reaction kinetics, see especially H.J. Schumacher, "Chemische Gasreaktionen," Die chemische Reaktion, Vol. III, Theodor Steinkopff, Dresden, 1938.

<sup>2</sup> If any conversion is given by an equation of the form (1), the chemical equation of gross conversion determines the reaction mechanism only in the rarest cases.

In principle, every reaction is reversible. In addition to the reaction represented by (1), the opposite reaction will also take place. Its velocity is

$$w' = + \frac{d[A]}{dt} = \dots = - \frac{\xi}{\alpha} \frac{d[X]}{dt} = k'[X]^{\xi}[Y]^{\eta} \dots \quad (3)$$

The resulting velocity according to (1),  $w_r$ , would then be

$$w_r = w - w' = k[A]^{\alpha}[B]^{\beta} \dots - k'[X]^{\xi}[Y]^{\eta} \dots \quad (4)$$

In reactions whose equilibrium is displaced far to one side (as in the case of extremely exothermal reactions with which we are dealing almost exclusively in this case) and in other reactions far from equilibrium, the opposite reaction can generally be disregarded, and (2) can be applied to the entire reaction velocity. We shall generally follow this practice. From (4) is derived the formal expression of the law of mass action for chemical equilibrium: In equilibrium, no conversion can take place, therefore

$$w_r = w - w' = 0 \quad (5)$$

and thus it follows from (4)

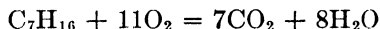
$$k[A]^{\alpha}[B]^{\beta} \dots - k'[X]^{\xi}[Y]^{\eta} \dots = 0; \quad \frac{[A]^{\alpha}[B]^{\beta} \dots}{[X]^{\xi}[Y]^{\eta} \dots} = \frac{k'}{k} = K \quad (6)$$

$K$ , the equilibrium constant of the law of mass action, is likewise still a function of the temperature. We can, by the way, express the concentrations in (2), (3), (4), and (6) by the partial pressures of the individual components. If we have measured the concentrations  $c_i$  in mols/liter, then  $v_i = 1/c_i$  is the volume that a mol of the substance occupies, and thus, according to the laws of gases,

$$p_i = \frac{RT}{v_i} = RTc_i \quad c_i = \frac{p_i}{RT} \quad (7)$$

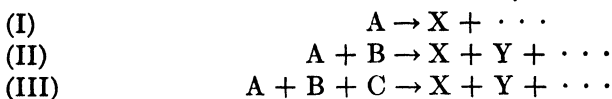
We usually include in the constant the power of  $RT$  remaining after substitution. In practical calculations, this must be taken into account.

If we are dealing with conversions of the type coming into consideration here, *e.g.*, the combustion of heptane



in which a total of 12 molecules takes part in the reaction, all the observations point to the fact that such a reaction equation cannot be determining for the velocity, but rather that the reaction must consist of a series of steps in each of which never more than three initial molecules take part at the same time. The probability that 12 molecules would collide in a definite configuration at the same time is so small as not to come into consideration for practical purposes. Of the multitude of reaction formulas conceivable according to (1), only three actually come into consideration. The actual multiplicity to be observed in the course of the reaction is due only to a combination of a series of such steps.

We need therefore consider only the following types of reaction:



which are designated according to the number of the initial molecules taking part as monomolecular, bimolecular, and trimolecular reactions.<sup>1</sup> For the velocity of the monomolecular reaction (I), the following is valid according to (2):

$$-\frac{d[A]}{dt} = k_1[A] \quad (8)$$

or, integrated,

$$-\ln \frac{[A]}{[A_0]} = k_1 t \quad (9)$$

if the concentration  $[A_0]$  occurs at the time  $t = 0$ . From this, then follows

$$[A] = [A_0]e^{-k_1 t} \quad (10)$$

If we plot the log of the concentration against the time in such a conversion, then, according to (9), we should obtain a straight line from the inclination of which  $k_1$  is computed. The time that passes till a definite portion has reacted can also serve as a measure of the velocity. Obviously, after the time  $\tau = 1/k_1$ , the concentration has dropped to  $1/e$  of its original value.  $\tau$  could be designated (as is done in the analogous radioactive disintegration processes) as the average life span of the initial products. Often the half-life period is taken as a measure of the velocity; *i.e.*, the time at which 50 per cent of the material is disintegrated, and which becomes, according to (9),

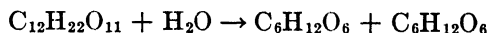
$$-\ln \frac{1}{2} = k_1 \tau_{1/2} \quad \tau_{1/2} = \frac{\ln 2}{k_1} = \frac{2.3 \log 2}{k_1} \quad (11)$$

Expressions for the "quarter-life period,"  $\tau_{1/4}$ , etc., could be derived and used in kinetic computations.

We shall understand by the "molecularity" of a reaction only what is predicated by Eqs. (I) to (III) concerning the number of initial molecules taking part in them, while we say that the time law (8), (9), or (10) designates a reaction of the first order. In general, we shall understand, by the order of a reaction, that power of the concentrations which goes into the formal law of time.

<sup>1</sup> The number of the reaction products appearing ( $X, Y, \dots$ ) is of no importance for our purposes here.

If we consider, for example, the inversion of cane sugar in a watery solution, namely, the conversion



then this is a bimolecular reaction in which a cane sugar and a water molecule take part. But, since water is practically always present in great excess and its concentration practically does not change during conversion, a velocity expression of the first order is found for this bimolecular reaction

$$-\frac{d[\text{C}_{12}\text{H}_{22}\text{O}_{11}]}{dt} = k[\text{C}_{12}\text{H}_{22}\text{O}_{11}]$$

For the bimolecular reaction (II), we should obtain the velocity equation of the second order

$$-\frac{dc_A}{dt} = \left(-\frac{dc_B}{dt}\right) = k_2 c_A c_B \quad (12)$$

If we designate the quantities present at the time  $t = 0$  by the above index 0 and state

$$x = c_A^0 - c_A = c_B^0 - c_B$$

where  $x$  is the converted mass, then

$$\frac{dx}{dt} = k_2(c_A^0 - x)(c_B^0 - x) \quad (13)$$

which, integrated, yields

$$\frac{1}{c_A^0 - c_B^0} \ln \frac{(c_A^0 - x)c_B^0}{(c_B^0 - x)c_A^0} = k_2 t \quad (14)$$

In case  $c_A^0 = c_B^0$ , we obtain, instead of (12), (13), and (14), the equation

$$\frac{dx}{dt} = k_2(c_A^0 - x)^2; \quad \frac{x}{(c_A^0 - x)c_A^0} = k_2 t \quad (15)$$

The half-life period becomes in the reaction of the second order in this case (the same concentration of both components)

$$\tau_{1/2} = \frac{1}{k_2 c_A^0}$$

If the half-life period of a reaction of the first order is compared with that of a reaction of the second order of the same initial velocity, in which therefore  $k_2 c_A^0 = k_1$ , the reaction of the second order must naturally have a longer half-life period than that of the reaction of the first order. For

<sup>1</sup>  $c_A$  is the same as  $[A]$ , etc.

the reaction of the second order, therefore,  $\tau_{1/2}^{\text{II}} = \frac{1}{k_2 c_A^0} = \frac{1}{k_1}$ ; and, for the reaction of the first order,  $\tau_{1/2}^{\text{I}} \cong 0.7/k_1$ .

To determine the order of a reaction, the time period found may be compared with that to be expected according to the above equations, especially with (10), (14), and (15). It is also possible to draw upon the values of the half-life and quarter-life periods. Frequently, however—and this might be the more reasonable course—we shall determine the concentrations in such small time intervals that we can, instead of (12), employ the approximate differential equation

$$-\frac{\Delta c_A}{\Delta t} \cong k_2 \bar{c}_A \bar{c}_B \quad (16)$$

in which  $\bar{c}_A$  and  $\bar{c}_B$  are the average concentrations in the time interval in question. This question can be compared directly with the experiment. In a reaction between an arbitrary number of molecules, we should determine the reaction velocity dependent on  $c_A$ ,  $c_B$ , etc., one after the other, keeping the initial concentrations of the other components constant. By the combination of all the observations, we finally obtain a velocity expression

$$\frac{dx}{dt} = f(c_A, c_B, c_C, \dots) \quad (17)$$

which in simple cases can also be reduced to the form

$$\frac{dx}{dt} = k' c_A^\alpha c_B^\beta c_C^\gamma \dots \quad (17a)$$

in which,  $\alpha$ ,  $\beta$ ,  $\gamma$ , . . . will frequently, but not necessarily always, be 1 or small whole numbers. In many cases, however, the velocity expression (17) cannot be reduced to the simplified form (17a). In all such cases, the interpretation of the determined formal velocity equation demands the construction of a more complicated reaction pattern, as we shall see later.

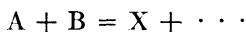
It is a matter of experience that the velocity of most of the reactions depends greatly upon the temperature. It is frequently stated as a rule that at room temperature an increase of  $10^\circ$  will almost double the velocity. To be sure, in some known cases, the velocity decreases with the temperature. If we plot the log of the reaction velocity against the reciprocal absolute temperature, we generally obtain a straight line; i.e., the coefficient of the reaction velocity as a function of the temperature is given by

$$k = A e^{-E/RT} \quad (18)$$

The simplest explanation of this expression is that only particularly energetic molecules are capable of reaction, those with an energy exceeding  $E$ , for which reason  $E$  is designated as "activation heat." We are led to an expression of the form of (18) as well by assuming that only collisions with sufficient kinetic energy of the relative movement of the molecules are effective as by assuming that only molecules with a certain minimum internal energy are capable of reaction (*cf.* pages 254*ff.*).

As has already been mentioned, many reactions do not take place according to a simple order. This may be explained by a complex reaction mechanism with a series of simple reactions. Many reactions apparently follow simple laws of the first, second, or third order, but these are in reality of a more complex nature. We shall come back to this in greater detail in a following section. We wish to point out a complication of a different kind that we shall also have to treat in greater detail, namely, the effect of the wall. All simple laws of gas reactions can be valid only as long as we are dealing with a homogeneous gas reaction. In practically all actual cases, the gas mixture is enclosed in walls, and it is a matter of experience that the border surface gas density can be of considerable influence on the reaction velocity. In studying and interpreting reactions, this may not be neglected.

**2. Kinetic Theory of Gases.**—In the preceding section, we introduced the velocity coefficients only as empirical factors, but it is especially important for practical computations to discuss the physical importance of these entities. If we proceed from the bimolecular reaction



in other words, an equation like  $H_2 + I_2 = 2HI$ , then, in a given gas mixture in a unit of time, no more molecules  $A$  and  $B$  can react with one another than collisions between them take place. In order to be able to state anything about this, we must make use of the fundamentals of the kinetic theory of gases. We must proceed from the fact that a gas consists of individual molecules, that these execute a chaotic heat movement, and that between the individual molecules there are moreover certain dynamic effects which, in the case of ideal gases, are negligible in finite intervals and which we express very roughly by thinking of them as completely elastic, rigid spheres between which an interaction repulsion occurs only during a collision.

In order to speak about the number of the collisions between the molecules, it is necessary first to gain information about the average velocity and the diameter of the individual particle. For determining the velocity, we shall proceed as follows: According to the kinetic theory of gases, the pressure of a gas must be caused by the impact of the molecules against the wall. The pressure is defined as force per unit of sur-



face; or, since force is the change of momentum (impulse) per second, the pressure equals the momentum transmitted by impacts of 1 cm<sup>2</sup> of surface during 1 sec. Let us imagine a parallelepipedal container, and let us assume for purposes of simplicity that one-third of all the molecules are moving back and forth in the direction of one of the corners, in other words one-sixth of all the molecules to a given surface. If  $w$  is the average velocity of the molecules, all the molecules will strike a surface of 1 cm<sup>2</sup> in 1 sec which were in a prism of 1 cm<sup>2</sup> surface and  $w$  cm in height and which flew in the right direction; thus, if  $n$  molecules are contained in 1 cm<sup>3</sup>,  $\frac{1}{6}nw$  molecules. If  $m$  is the mass of the individual molecule and  $mw$  its momentum, then, instead of the momentum  $mw$ ,  $2mw$  is transmitted to the wall with the elastic impact, since the direction of the original momentum is reversed after the impact. The striking molecule has the momentum  $mw$  before the impact, after the impact  $-mw$ ; the change of the momentum is thus  $2mw$ . The total momentum transmitted to 1 cm<sup>2</sup>/sec therefore becomes

$$p = \frac{1}{3}nmw^2 \quad (19)$$

If in the volume  $V$  of the gas there is contained 1 mol =  $N_L$  molecules then  $n = \frac{N_L}{V}$  and thus

$$p = \frac{1}{3} N_L \frac{mw^2}{V}$$

If we take into account that  $N_L m = M$ , the mass of a mol, then

$$pV = \frac{1}{3}Mw^2 = \frac{2}{3}E_{\text{kin}} \quad (20)$$

where  $E_{\text{kin}}$  is the kinetic energy of the gas  $\left(E_{\text{kin}} = \frac{M}{2}w^2\right)$ . Comparison with the usual form of the law of gases

$$pV = RT$$

yields

$$\frac{1}{3} Mw^2 = RT \quad w^2 = \frac{3RT}{M} \quad (21)$$

(21) furnishes us with one of the first relations for computing  $\bar{w}^2$ :

$$\sqrt{\bar{w}^2} = \sqrt{\frac{3RT}{M}} \cong 15,800 \sqrt{\frac{T}{M}} \text{ cm/sec} \quad (22)$$

in which  $M$  is the molecular weight. We note that (20) is correct in spite of our simplifying assumptions, if  $\bar{w}^2$  represents the average value of the square of the velocity. For an exact computation, it would be necessary to consider all the directions of flight of the molecules and all

velocities coming into consideration and to find the average value for them. We should then have obtained (20) with the given meaning of  $w^2$ . We merely note here what we can show, like the close calculation necessary for the foregoing, only by means of Maxwell's law of velocity distribution to be derived below, namely, that for the average value of the velocity itself the following results:

$$\bar{w} = \sqrt{\frac{8RT}{\pi M}} = 14,500 \sqrt{\frac{T}{M}} \text{ cm/sec} \quad (22a)$$

(therefore differing from  $\sqrt{w^2}$  only by a numerical factor deviating but little from unity).

Molecular velocity therefore normally has values of several hundred meters per second.

A certain point of contact for the molecular diameter is furnished by the values for the volume correction which appears in van der Waals' equation, or from the mol-volume of solid materials. It develops that the molecular diameter must be of the order of magnitude of several Å ( $= 10^{-8}$  cm). Establishing the molecular cross section in the gas itself is possible on the basis of all those properties which depend on the "free path length" of a particle. By average free path length is meant that distance which a gas particle must travel on the average until it collides with another. Naturally, this distance is shorter the more molecules there are in a  $\text{cm}^3$  and the greater their cross section; in other words, we should expect

$$\lambda \cong \frac{1}{n\pi\sigma^2} \quad (23)$$

where  $\sigma$  is the molecular diameter<sup>1</sup> and  $n$  the number of molecules per  $\text{cm}^3$ . The exact computation, which we do not wish to perform here, yields in (23) an additional numerical factor of the order of magnitude of unity.

The phenomena that depend on the free path length are internal friction, heat conduction, and diffusion, which are taken together as transport problems, *i.e.*, transport of momentum, of energy, and of material. In all three cases, a molecule transports the entity in question more rapidly the greater the free path length. In the case of viscosity and conduction, however, the number of molecules present, which is inversely proportional to the free path length, exactly compensates for

<sup>1</sup> If two molecules, each of which has the radius  $r = \sigma/2$ , collide, it is possible to present this formally in the following manner: We regard one as a point and attribute to the other a radius of  $2r = \sigma$ . If the thrusting pointlike particle enters the circle of the surface  $\pi\sigma^2$  around the center of the second particle, a collision takes place; hence, in (23),  $\sigma^2$  and not  $r^2$ . In a collision of different kinds of molecule,  $\sigma$  equals the sum of the various radii.

this factor so that these entities are independent of the pressure.<sup>1</sup> The case is different in diffusion when it depends on the mobility of the individual particle and is therefore inversely proportional to the pressure.

Of the quantitative relations for these entities, we shall mention only those of diffusion, since diffusion phenomena are important in many flames and in oxidation reactions in the presence of walls. The simplest case is that of diffusion within itself, auto-diffusion; *i.e.*, in a quantity of gas, imagine a number of the molecules as marked ("painted red") and then observe their temporal distribution among the rest. This situation can today be realized experimentally, if isotopes are taken<sup>2</sup> as the "marked" molecules. The simplest expressions for the diffusion constants are given by

$$D \cong \frac{\lambda \bar{w}}{3} \quad (24)$$

From this,  $D$  can be derived from known  $\lambda$ ; conversely, internal friction  $\eta$  can be derived from (24) or from the similar formula for  $\eta$

$$\eta = \frac{\rho \bar{w} \lambda}{3} \quad (25)$$

where  $\rho$  is the density.

The  $\lambda$  values as well as the molecular diameters derived from them can be found in tabulations. In the diffusion of two different gases in one another, there are complicated expressions for  $D$ . The simplest expressions are furnished by an equation analogous to (24) and symmetrical in the components 1 and 2

$$D \cong \frac{n_1 \bar{w}_2 \lambda_2 + n_2 \bar{w}_1 \lambda_1}{3(n_1 + n_2)} \quad (26)$$

From this, it is clear that (24) with average values for  $\lambda$  and  $\bar{w}$  will give good results for approximate preliminary estimates.

For the number of collisions, which is to be estimated for the simplest case, *i.e.*, the number of impacts of a molecule with its own kind, we

<sup>1</sup> Always considering that the pressure is so high that the free path length remains small compared with the dimensions of the container—in general, therefore, at pressures of several millimeters upward.

<sup>2</sup> Auto-diffusion is obtained only if the mass difference of the isotopes is small. The diffusion of hydrogen in deuterium does not yield the coefficient of auto-diffusion because of the great mass difference. But the diffusion of HI in DI does yield that of auto-diffusion in HI, because in this compound the relative mass differences are very small.

obtain as the distance ( $= \bar{w}$ ) covered, divided by the free path length

$$Z \cong \frac{\bar{w}}{\lambda} \quad (27)$$

It should be recalled that  $\bar{w}$  becomes several  $10^4$  cm/sec for gases of average molecular weight (approximately between 10 and 100). For  $\lambda$  in the case of molecules of several angstroms diameter at atmospheric pressure, we obtain  $10^{-5}$  to  $10^{-6}$  cm; for  $Z$ , therefore,  $10^9$  up to  $10^{10}$  impacts per second. It is convenient to keep this order of magnitude in mind.

The above formulas require further refinement. We shall return to them later and shall give the more exact formulas without going into the details of the computation.

The most essential simplification contained in our previous considerations is the assumption of the same velocity for all molecules. It is clear, however, that such an equal distribution of velocity, even if it were artificially advanced at the start, cannot be stable, but rather that, by the collision of the gas molecules with one another, important deviations from regularity must occur.<sup>1</sup>

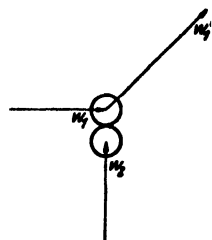


FIG. 157.

A second assumption, less questionable from the standpoint of reaction kinetics, was the above conception employed to derive the pressure, that one-third of all the molecules move in one of three directions perpendicular to each other. From this, we obtained the expression

$$p = \frac{1}{3}nmw^2$$

for the pressure, which was correct in spite of the fact that the assumption was in itself unallowable, whereas an incorrect value results for the number of impacts against 1 cm<sup>2</sup> of wall per second. For this, we had obtained  $\frac{1}{6}n\bar{w}$ , and the exact computation yields  $\frac{1}{4}n\bar{w}$ .\*

We shall now attempt to correct for the first assumption, namely, that there is an equal distribution of velocity. We shall not proceed historically but rather shall begin with the cases of discontinuous energy distribution that are yielded by the quantum theory and then refer to a continuous energy distribution and thus also draw upon Maxwell's law of velocity distribution. Naturally, we shall not be able to account theoretically for all the steps involved and shall therefore occasionally refer to special works on the subject. We shall begin with the observed

<sup>1</sup> Cf., e.g., HERZFELD, "Kinetische Theorie," pp. 11ff. If two molecules of the same mass and of equal velocity collide in the manner shown by Fig. 157, molecule 1 will possess the entire energy and 2 will remain stationary. The collisions therefore actually cause great deviations from an originally equal distribution of velocity.

\* The difference of one-sixth as opposed to one-fourth can also be disregarded for many reaction-kinetic considerations.

fact that atoms and molecules, disregarding their translation energy (the kinetic energy of the movement of the center of gravity), can be in a number of discrete energy conditions which, to be sure, except in special cases, are not straight whole-numbered multiples of a definite minimum energy but whose amount is given by expressions that are multiples of effect quantum ( $= 6.56 \cdot 10^{-27}$  erg cm) and whole numbers. The existence of such discrete energy conditions is proved directly by the Franck-Hertz experiments on electron impacts.<sup>1</sup> It also follows from spectroscopic facts and from other data. If electrons are permitted to collide with atoms and if the electrons are given specific energies in known fields, velocity losses of the electrons always occur from definite energy stages that correspond to the stages of the internal energy of the atom. In atoms, the various conditions derive from the various energies with which the electrons can move in the nuclear field. In the case of molecules, there is also the energy oscillation of the individual atoms against one another as well as the energy of the rotation of the entire molecule and even parts of it, all of which are "quantumed."

For what follows, it is as yet of no importance what laws describe the discrete energy conditions of a system. It is only of interest that such a series of discrete energy conditions  $\epsilon_0, \epsilon_1, \epsilon_2, \dots$  exists, a fact that is supported by the Franck-Hertz experiments and the spectroscopic results. To do justice to the facts, it is necessary to make the probability of the  $i$ th energy condition proportional to

$$g_i e^{-\epsilon_i/kT} \quad (28)$$

where  $g_i$  is the so-called "quantum weight" and is always a small whole number, frequently 1.<sup>2</sup> The appearance of the weight factor derives from the fact that there are often a number of different conditions with the same energy  $\epsilon_i$  (in such cases, we speak of degeneration).  $g_i$  is simply the number of such conditions compared with the same total energy, and it is often more convenient to compute with Eq. (28) instead of taking all the degenerate conditions individually.

We shall here omit an analysis of (28).<sup>\*</sup> We wish only to show that by applying (28) to only two conditions, 0 and 1, we arrive at the same result as with the usual elementary thermodynamic equilibrium computation. If we designate the numbers of the particles in condition 0 with  $A_0$  and those in condition 1 with  $A_1$ , we should have the following reaction equation for the equilibrium:



<sup>1</sup> Cf. FRANCK, J., and P. JORDAN, "Anregung von Quantensprüngen."

<sup>2</sup>  $k = R/N_L$ , in other words, the gas constant related to the individual molecule.  $\epsilon_i$  also refers to the individual molecule and not to a mol.

<sup>\*</sup> Cf., e.g., HERZFELD, K.F., "Kinetische Theorie," Brunswick, 1925.

where the heat production (computed for the individual molecule) =  $(\epsilon_0 - \epsilon_1) = -\Delta\epsilon$ .

Applying van't Hoff's equation<sup>1</sup> with the equilibrium constant  $K = \frac{A_1}{A_0}$  yields

$$\frac{d \ln K}{dT} = \frac{\Delta\epsilon}{kT^2} \quad (30)$$

Since in our case  $\Delta\epsilon$  is independent of the temperature, only the difference of the "chemical constant" for  $A_1$  and  $A_0$  appears as a constant in the integration.<sup>1</sup> Since  $A_0$  and  $A_1$  are differentiated only by their stimulus condition, only the members  $\ln g_1$  and  $\ln g_0$  of the quantum weights remain for the chemical constants.<sup>2</sup> We thus obtain

$$\ln K = -\frac{\Delta\epsilon}{kT} + \ln g_1 - \ln g_0 \quad (31)$$

or

$$K = \frac{A_1}{A_0} = e^{-\Delta\epsilon/kT} \frac{g_1}{g_0} = \frac{g_1 e^{-\epsilon_1/kT}}{g_0 e^{-\epsilon_0/kT}} \quad (32)$$

which coincides with the direct result of (28).

The above presentation is not entirely consistent, since statements on the chemical constants have been arrived at only by an application of statistics. Here we are more concerned with showing the connection with familiar relations.

In the case of the harmonic oscillator, the result of the energy conditions is especially simple. By a harmonic oscillator is meant a mass point that executes harmonic oscillations. As a preliminary approximation, an oscillating biatomic molecule can be regarded as a harmonic oscillator; here, therefore, the two atoms oscillate against one another. We find that a harmonic oscillator is capable only of the succession of the energy conditions

$$nh\nu$$

where  $\nu$  is its own frequency,  $n$  is a whole number, and  $h$  is again Planck's effective quantum. The more exact theory shows that, instead of  $n$ , it should be  $(n - \frac{1}{2})$  and that the lowest condition is not the one without oscillation but that with an energy content of a half "oscillation quant." At this point, this difference plays no role because we are here concerned only with energy differences. The number of particles in the  $n$ th energy condition will then be

$$Ae^{-nh\nu/kT} \quad (33)$$

If we have a system of  $N$  oscillators, then obviously

$$N = \sum_{n=0}^{\infty} Ae^{-nh\nu/kT}$$

for if we sum up the numbers of the particles in all possible energy conditions, we must obtain all the particles, or, since it is simply a matter of

<sup>1</sup> Cf. textbooks on physical chemistry.

<sup>2</sup> Cf., for example, ШОТТК, W., "Thermodynamik," Berlin, 1929.

the summation of a geometrical series in this case,

$$N = A \frac{1}{1 - e^{-h\nu/kT}} \quad A = N(1 - e^{-h\nu/kT})$$

The fraction of the molecules in the  $n$ th energy condition therefore becomes

$$\Delta N = N(1 - e^{-h\nu/kT})e^{-nh\nu/kT} \quad (34)$$

and the sums  $N_0$  of all the molecules with energies  $\geq \epsilon_0 = n_0 h\nu$

$$N_0 = N(1 - e^{-h\nu/kT}) \sum_{n=n_0}^{\infty} e^{-nh\nu/kT} = \frac{N(1 - e^{-h\nu/kT})e^{-n_0 h\nu/kT}}{1 - e^{-h\nu/kT}}$$

$$N_0 = N e^{-n_0 h\nu/kT} = N e^{-\epsilon/kT} \quad (35)$$

If, in a system of oscillators, only those with an energy  $\geq \epsilon_0 = n_0 h\nu$  are capable of reaction, the fraction expressed by (35) should be inserted. If two such molecules collide and we assume that reaction could take place if the entire oscillating energy of the two molecules together is greater than or equal to  $\epsilon_0$ , the fraction of the successful impacts will be considerably greater than the fraction (35); for the total energy  $n_0 h\nu$  can already be realized in the following  $(n_0 - 1)$  various ways: The first molecule can contain  $n_0$ , and the second 0 oscillation quanta; further, the first  $(n_0 - 1)$ , the second 1, etc. The exact expression for the fraction of successful impacts thus resulting can be given (*cf.* page 256). At this point, it suffices to note that the "Boltzmann factor"  $e^{-\epsilon/kT}$  need give the fraction of molecules capable of reaction only approximately.

We now wish to compute the distribution function for the kinetic energy of a gas. We wish to know how many molecules are contained in a given volume element and how the distribution of their velocities  $v$  is according to size and direction.

In a continuous energy distribution, it is meaningless to ask about the number of particles that have a definite velocity  $v$  (or right-angled components of the velocity  $v_x, v_y, v_z$ ) or a definite energy  $\epsilon = \frac{m}{2} v^2$ , if  $m$  is the mass of the particles. It is meaningful only to ask how many particles have velocity whose components lie between  $v_x$  and  $v_x + dv_x$ ,  $v_y + dv_y$  and  $v_z + dv_z$  or whose kinetic energy lies in a corresponding interval. It is natural to state the fraction  $dN'$  of particles whose velocities lie in the interval in question thus

$$dN' \text{ proportional } N e^{-\epsilon/kT} dv_x dv_y dv_z, \quad (36)$$

if  $N$  is the total number of the particles and

$$\epsilon = \frac{m}{2} v^2 = \frac{m}{2} (v_x^2 + v_y^2 + v_z^2) \quad (37)$$

the kinetic energy of the velocity  $v$ . Since we are interested only in the amount of velocity and not in its direction (the velocities of the individual molecules will be distributed chaotically in space), we proceed from the right-angled components to those in polar coordinates ( $v, \vartheta, \varphi$ ), and, instead of (36), we obtain

$$dN' = ANe^{-(m/2)(v^2/kT)}v^2 \sin \vartheta \, d\vartheta \, d\varphi \, dv \quad (38)$$

By integration of all possible values of  $\vartheta$  and  $\varphi$ , we obtain the number  $dN$  of the particles with velocities between  $v$  and  $v + dv$ , independent of the direction. The proportionality factor  $A$  is then determined, as was done above (p. 254), from the conditions that integration of  $dN$  of all possible values of  $v$ , that is, of 0 to  $\infty$ , must yield the total number  $N$  of the particles present.<sup>1</sup>

Thus we finally obtain the desired form of Maxwell's law of velocity distribution

$$dN = 4\pi N \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-mv^2/2kT} v^2 \, dv \quad (39)$$

A stricter analysis for the above-treated examples would demand the use of this equation.  $dN/N$  is therefore the fraction of the particles that have a velocity between  $v$  and  $v + dv$ . We shall here give only the more exact value for the number of impacts between two kinds of molecules 1 and 2 with masses  $m_1$  and  $m_2$  and diameters  $\sigma_1$  and  $\sigma_2$ . Of these, let  $N_1$  and  $N_2$ , respectively, be present in a cubic centimeter; this value is

$$Z_{12} = 2N_1N_2 \left( \frac{\sigma_1 + \sigma_2}{2} \right)^2 \left[ \frac{2\pi kT(m_1 + m_2)}{m_1m_2} \right]^{1/2} \quad (40)$$

If only one type of molecule is present, the number of the impacts becomes

$$Z = N^2\sigma^2(4\pi kTm)^{1/2} \quad (41)$$

(Factor 2 is dropped, since otherwise every impact would be counted twice, each molecule once as giving the impact and once as receiving it.)

Numerical values of  $\sigma$  for the purpose of a more exact computation of  $Z$  can be obtained from tables. As an approximation, it suffices for most purposes that a molecule receives about  $10^9$  to  $10^{10}$  impacts per second under normal conditions (*cf.* page 251).

For reaction-kinetic purposes, as we shall see, the impacts with a certain minimum energy, about  $\geq E_0$  (referring to a mol), are of interest, especially the kinetic energy of the movement of both impact partners relative to each other. We then obtain for the number of these impacts  $[Z(E_0)]$ , disregarding minor refinements,

$$Z(E_0) = Ze^{-E_0/RT} \quad (42)$$

<sup>1</sup> For details of computation and a more exact derivation, we refer to special works like Herzfeld, "Kinetische Theorie."



where  $Z$  is the given number of impacts above. The empirically discovered temperature dependence on the part of reaction velocities can thus be accounted for directly by the fact that only those molecules react which possess a certain minimum energy at impact. The kinetic energy of translation (the movement of the center of gravity of the molecule) is not the only energy a molecule possesses, however. The molecule (disregarding monoatomic molecules) can also rotate, and the individual atoms in the molecule can execute oscillations compared with one another. Similar forms of the law of energy distribution are valid for rotation and oscillation energy, as we have pointed out. It can therefore also occur that an empirically discovered velocity expression of the form (42) states: Two molecules react with one another when one of them has an oscillation energy  $\geq E_0$  (we disregard the effect of the rotation energy, since there is reason to assume that the latter plays a smaller role in the activation of chemical reactions than does oscillation).

Just as in the observations made above (page 253), the following is also conceivable: If it is necessary to produce an activation energy  $\geq E_0$ , it could be that one molecule has the oscillation  $\epsilon$  and the other an energy  $\geq (E_0 - \epsilon)$ . It can be seen without computation that there must be a great number of possibilities by which the energy  $\geq E_0$  comes about; and as a result the probability of activation, according to this mechanism, must be greater by a certain factor than  $e^{-E_0/RT}$ ; in the above example, it becomes

$$\sim \frac{E_0}{RT} e^{-E_0/RT}$$

If  $E_0$  is about twenty to fifty times  $RT$ , the additional factor becomes about 20 to 50. If not two, as in the above case, but  $n$  degrees of freedom oscillation take part (multiatomic molecules possess a great number of degrees of freedom oscillation), then instead a factor

$$\left(\frac{E_0}{RT}\right)^{n-1} \frac{1}{(n-1)!} \quad (43)$$

would result, which, under certain circumstances, would amount to many powers of 10. Such factors play a considerable role, especially in monomolecular reactions.

In a monomolecular reaction, the fraction  $e^{-E_0/RT}$  of molecules high in energy disintegrates, the energy distribution is disturbed,<sup>1</sup> and the disintegration can proceed only if new molecules are activated. The collision of molecules is, however, a bimolecular process; as a result, the monomolecular disintegration of the molecules can proceed according to a law of the first order only if the disintegration takes place slowly compared with the activation by impacts. The number of impacts at atmospheric pressure is, as we have seen, of the order of magnitude  $10^9$  to  $10^{10}$  per second. The duration between two impacts would thus have

<sup>1</sup> But especially the molecules rich in energy will be absent.

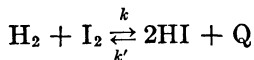
to be  $10^{-9}$  to  $10^{-10}$  per second; and, compared with this time, the life span of an activated particle would have to be long. As velocity coefficients of monomolecular reactions,  $ke^{-E/RT}$ , we frequently find numerical values where  $k$  is about  $10^{13}$  to  $10^{15}$ . As the "life span" of an activated particle, only  $10^{13}$  to  $10^{15}$  sec would result from this; in other words, this is by no means a long time as compared with the duration between two impacts. This difficulty disappears only if we assume that in activation a greater number of degrees of freedom is involved because then the number of activated molecules is considerably higher.

In addition to a factor greater than unity determined by the participation of several degrees of freedom, so-called "spatial factors"  $< 1$  can appear in bimolecular reactions. If two molecules collide, their orientation to each other at the impact is important for the reaction. In the reaction  $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$ , an impact  $\begin{smallmatrix} \text{H—I} \\ \text{H—I} \end{smallmatrix}$  will perhaps be able to lead to the formation of the end products, but an impact certainly will not in which the molecules are oriented in the following way:



In a reaction like  $\text{H} + \text{HI} \rightarrow \text{H}_2 + \text{I}$ , certainly only such impacts will be effective in which the H-atom strikes the HI-molecule on the "H-side," etc. It is therefore not surprising that we find such numerical factors  $< 1$ , steric (spatial) factors, although relatively little is still known about the more exact values of steric factors.

If we consider the velocity of the forward and reversed reaction of a given conversion, let us say,



where  $Q$  is the heat production, then the following is valid:

$$k = Ae^{-E/RT}; \quad k' = A'e^{-E'/RT}$$

For the equilibrium constants,<sup>1</sup> the following is valid  $\left(K = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2}\right)$ :

$$\frac{d \ln K}{dT} = \frac{Q}{RT^2}; \quad \log K \cong -\frac{Q}{RT} + \text{const}$$

Further, as we have seen above (page 242),

$$K = \frac{k'}{k}$$

<sup>1</sup> Cf. textbooks of physical chemistry.

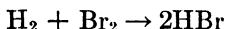
If the above values are given for  $k$ ,  $k'$ , and  $K$ , it follows:

$$Q = E' - E$$

the difference of the activating heat in the forward reaction and the reverse reaction is equal to the heat production of this reaction. In the above example,  $Q$ , for instance, is known from thermochemical data,  $Q \cong 2.7$  kcal; Bodenstein<sup>1</sup> found that  $E = 38.8$  kcal and that  $E' = 43.8$  kcal; hence  $E' - E = 5.0$  kcal. Since the reaction heats can in general be assumed as known as well as the equilibrium constants, it is possible to make statements about a reaction even though only its reverse reaction has been studied.

Other reaction-kinetic relations that are needed, especially the laws of chain reactions, can best be learned from examples. Since of all the reactions taking place in combustion none is so simple and so completely known in detail as the hydrogen bromide reaction, we shall begin with this simple case.

**3. Chain Reactions Illustrated by the Example of the Reaction between Bromine and Hydrogen.**—For the velocity of the formation of hydrogen bromide



it was found experimentally by Bodenstein and Lind<sup>2</sup>

$$\frac{d[\text{HBr}]}{dt} = \text{const} \frac{[\text{H}_2] \sqrt{[\text{Br}_2]}}{1 + m \frac{[\text{HBr}]}{[\text{Br}_2]}} \quad (44)$$

in which  $m \cong 10$ .\*

An interpretation of this velocity expression was given independently by Christiansen<sup>3</sup> and Polanyi<sup>4</sup> and Herzfeld.<sup>5</sup> According to them, the conversion is brought about by the reaction of bromine atoms, whose concentration in thermal equilibrium is  $\sim \sqrt{[\text{Br}_2]}$ , with  $\text{H}_2$ -molecules. This yields the expression in the numerator of (44). In the reaction of a bromine atom with a hydrogen molecule, an  $\text{HBr}$ -atom and an  $\text{H}$ -atom are formed. The  $\text{H}$ -atom can now continue to react with a bromine molecule to form  $\text{HBr}$  with regeneration of the  $\text{Br}$ -atom which had origi-

<sup>1</sup> BODENSTEIN, M., *Z. physik. Chem.*, **13**, 56 (1894); **22**, 1 (1897); **29**, 295 (1898).

<sup>2</sup> BODENSTEIN, M., and S.C. LIND, *Z. physik. Chem.*, **57**, 116 (1906).

\* According to a later investigation by Bodenstein and Jung [*Z. physik. Chem.*, **121**, 127 (1926)],  $m = 8.4$  independently of the temperature.

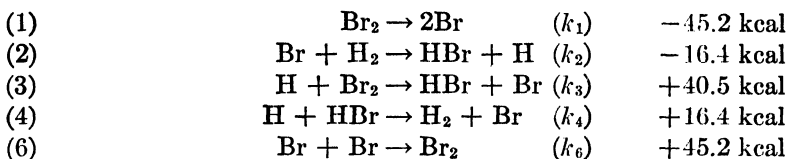
<sup>3</sup> CHRISTIANSEN, J.A., *Kgl. Danske Videnskab. Selskab Math. fys. Medd.* **I**, 14 (1919).

<sup>4</sup> POLANYI, M., *Z. Elektrochem.*, **26**, 50 (1920).

<sup>5</sup> HERZFELD, K.F., *Ann. Physik*, **57**, 635 (1919). *Z. Elektrochem.*, **25**, 301 (1919).

nally entered the reaction, but it can also react with HBr with retrogressive formation of  $H_2$  and likewise a regeneration of the Br-atom. The combination of HBr by H-atoms means an inhibition of the reaction, hence the expression in the denominator of (44). The smaller the quotient  $[HBr]/[Br_2]$  the smaller the inhibition of the reaction by HBr, for the fraction of the H-atoms that react with HBr and not with  $Br_2$  is so much smaller. The formation of the velocity expression (44) will now be considered in detail, and at the same time the photochemical reaction will be considered (Bodenstein and his associates). This has contributed materially to the understanding of the details of the mechanism concerned.<sup>1</sup>

For hydrogen bromide formation, the following "pattern" is valid:



Such a reaction is called a "chain reaction." The following is characteristic for such a reaction: There is a "chain-inducing" reaction (1) according to which, by the dissociation of a bromine molecule, free bromine atoms are formed that continue the chain. Experience teaches that free atoms are especially capable of reaction, just as are free radicals. The bromine atoms formed according to (1) can react according to (2), giving rise to a new active particle to make up for the disappearing Br-atom, namely, the H-atom, which on its part reacts according to (3) or (4) by the retrogressive formation of a Br-atom. In this "reaction chain," no active particles are combined, and the chain would become infinitely long and the number of the Br-atoms and therefore the reaction velocity would become infinitely great, if the recombination of two bromine atoms were not added as "chain-breaking" reaction (6).

Practically, there is no way of assigning this chain pattern to an empirical reaction equation. It is necessary, rather, to construct a plausible pattern, to derive the reaction equation resulting from it, and then to compare this with experience.

From the above pattern, the reaction equation is obtained according to Bodenstein in the following way: Hydrogen bromide is formed according to Eqs. (2) and (3) and combines according to (4); the resulting formation velocity is

$$\frac{d[HBr]}{dt} = k_2[Br][H_2] + k_3[H][Br_2] - k_4[H][HBr] \quad (45)$$

<sup>1</sup> BODENSTEIN, M., and H. LÜTKEMEYER, *Z. physik. Chem.*, **114**, 208 (1924).

In this, the unknown concentrations  $[\text{Br}]$  and  $[\text{H}]$  appear. For  $[\text{Br}]$ , the equilibrium concentration of the bromine atoms  $[\text{Br}] = \sqrt{K[\text{Br}_2]}$  could simply be inserted in the case of the thermal reaction, where  $K$  is the equilibrium constant of the reaction  $\text{Br}_2 \rightleftharpoons 2\text{Br}$ . For the sake of general validity, however, and in order that the final formula obtained might also be applicable to the photochemical reaction, we shall explicitly compute by the above method. For the formation velocity of the free atoms, we obtain from the pattern

$$\begin{aligned} \text{(I)} \quad \frac{d[\text{Br}]}{dt} &= 2k_1[\text{Br}_2] - k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}] \\ &\quad - 2k_6[\text{Br}]^2 \\ \text{(II)} \quad \frac{d[\text{H}]}{dt} &= k_2[\text{Br}][\text{H}_2] - k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}] \end{aligned}$$

For the static reaction, Bodenstein assumes "quasistationarity" of the concentrations of the active particles and therefore gives the two preceding expressions as equal to zero. This assumption would be exactly correct if one kept the concentrations of the reaction participants constant (*e.g.*, by means of adding and withdrawing, through semipermeable walls). Under practical conditions, however, it is exact enough to warrant its use.

If, therefore,  $\frac{d[\text{H}]}{dt} = \frac{d[\text{Br}]}{dt} = 0$ , it follows by subtraction of the above expressions that

$$\begin{aligned} 2k_1[\text{Br}_2] - 2k_6[\text{Br}]^2 &= 0 \\ [\text{Br}] &= \sqrt{\frac{k_1}{k_6} [\text{Br}_2]} \end{aligned} \quad (46)$$

$k_1/k_6$ , the relation of the velocity constants for the reaction forward and reverse, is equal to the equilibrium constant  $K$ . As stated above, one therefore obtains in the thermal reaction  $[\text{Br}] = \sqrt{K[\text{Br}_2]}$  (photochemical reaction; *cf.* page 262).

For [II], we obtain from Eq. (II)

$$[\text{H}] = \frac{k_2[\text{Br}][\text{H}_2]}{k_3[\text{Br}_2] + k_4[\text{HBr}]} \quad (47)$$

and, with the above value for  $[\text{Br}]$ ,

$$k_2[\text{Br}_2] + k_4[\text{HBr}] \quad (48)$$

Employing these two expressions for  $[\text{Br}]$  and  $[\text{H}]$ , we obtain

$$\frac{d[\text{HBr}]}{dt} = k_2[\text{H}_2] \sqrt{\frac{k_1}{k_6} [\text{Br}_2]} \left\{ 1 + \frac{k_3[\text{Br}_2] - k_4[\text{HBr}]}{k_3[\text{Br}_2] + k_4[\text{HBr}]} \right\}$$

The reaction velocity therefore becomes

$$\frac{d[\text{HBr}]}{dt} = \frac{2k_2[\text{H}_2] \sqrt{\frac{k_1}{k_6} [\text{Br}_2]}}{1 + \frac{k_4}{k_3} \frac{[\text{HBr}]}{[\text{Br}_2]}} \quad (49)$$

This velocity expression is clearly identical with that discovered empirically by Bodenstein and Lind, if

$$\frac{k_4}{k_3} = \frac{1}{8.4}$$

Such a reaction pattern, formally derived and furnishing the correct gross reaction equation, is meaningful only if the individual velocity constants also assume physically reasonable values. Since, in the above radical expression, the known equilibrium constant of the  $\text{Br}_2$ -dissociation equilibrium is included,  $k_2$  can be computed from the empirically discovered velocity expression, and it will be found, if the concentrations are expressed in mols/cm<sup>3</sup>, that

$$k_2 = 4.55 \cdot 10^{13} e^{-17,600/RT}$$

The impact number of Br and  $\text{H}_2$  is computed at the experimental temperature of  $\sim 200^\circ\text{C}$  at  $Z \cong 2 \cdot 10^{14}$  (as the order of magnitude for  $Z$  at atmospheric pressure, we have previously given  $10^9$  to  $10^{10}$ ; 1 mol is contained in 22.4 liters; for 1 mol/cm<sup>3</sup> as a unit of concentration, a value for  $Z$  consequently results that is  $\sim 2 \cdot 10^4$  times larger).  $k_2$  is therefore of the order of magnitude of the impact number, in addition to which a spatial factor  $\sim \frac{1}{5}$  could be included. The activation heat of 2 of 17.6 kcal is nearly exactly equal to the heat production of this endothermic reaction. From this, it would follow that the activation heat of the reversed exothermic reaction of H with HBr is in this case practically equal to zero (*cf.* page 258).

This assumption, namely, that for exothermal atomic reactions the activation heat is generally zero, was introduced in 1919 by Herzfeld but later dropped again. Experience in the meantime has shown that the activation heats of exothermal atomic reactions are, to be sure, not exactly zero but are in general quite small,<sup>1</sup> and that it is therefore possible, within certain limits, to make predictions about the velocity of atomic reactions of the type discussed. It is possible to say that the activation heats of exothermal atomic reactions are generally only

<sup>1</sup> *Cf.* GEIB, K.H., Atomreaktionen, *Ergeb. exakt. Naturw.*, **15**, 44 (1936).

several kcal (up to  $\sim 10$ ), and those of endothermal atomic reactions in general are about as many kcal above the heat production.

The hydrogen bromide reaction, however, permits several additional conclusions which are of importance also in other respects and which we shall treat here. If the reaction is investigated photochemically, it is seen that a molecule of  $\text{Br}_2$  is split up into atoms in the suitable spectrum range for an absorbed light quantum.<sup>1</sup> Instead of  $2k_1[\text{Br}_2]$ , the velocity of the formation of free atoms in the thermal case, there must appear  $2I_{\text{abs}}$ , if  $I_{\text{abs}}$  is the absorbed light energy expressed in "molquanta" ( $6 \cdot 10^{23}$  quanta) per  $\text{cm}^3$ . Now the experimentally established reaction velocity in light<sup>2</sup> permits us to compute the constant  $k_6$ , since  $k_2$  is already known from the thermal experiments. For this, we find, if the concentrations are again computed in  $\text{mol}/\text{cm}^3$ ,

$$k_6 = 2.5 \cdot 10^{11}$$

if the experiments have been carried out at atmospheric pressure. But this is by no means equal to the impact number among Br-atoms related to  $\text{mol}/\text{cm}^3$  as the unit of concentration, for which we compute about  $5 \cdot 10^{13}$ . This means, however, that only about every two hundredth impact between bromine atoms leads to recombination.<sup>2</sup>

The fact first observed by Bodenstein and Lütkemeyer, that in a recombination reaction there is a yield of only about  $1/1000$ , did not come as a complete surprise. Herzfeld had already pointed out that the newly formed molecule  $\text{Br}_2$  still contains the entire reaction heat and therefore can disintegrate again immediately. A  $\text{Br}_2$  "quasimolecule" formed by impact of two Br atoms will therefore generally disintegrate again after a life span that is comparable with the oscillation duration of the molecule of  $\sim 10^{-13}$  sec, unless it has occasion during this life span to give off its energy, or at least a part of it, in collision with another molecule. The fraction of the "effective" impacts between bromine atoms is therefore approximately given (as long as the pressure is not too high) by the ratio of the time span of the quasimolecule to the time between two impacts of the quasimolecule with a foreign molecule. (It is not necessary to introduce the concept of the "quasimolecule." It may be said instead more simply: Two atoms recombine only in a triple collision, in which a triple collision is understood to be an impact in which within a short time of  $\sim 10^{-13}$  sec a third collision partner is added to the collision pair.) This ratio is, however, proportional to the pressure, and it is therefore necessary to find proportionality for the velocity of the recombination

<sup>1</sup> This takes place on the observed spectrum.

<sup>2</sup> BODENSTEIN, M., and H. LÜTKEMEYER, quoted p. 259. HERZFELD, K.F., quoted p. 259.

of two free atoms with the pressure of foreign gases present; and this is actually the case.<sup>1</sup> (In the thermal reaction, this pressure effect does not appear, since the disintegration of the added foreign gas is influenced in the same manner as the recombination. If this were not so, a displacement of the equilibrium would result with the addition, and this would be in contradiction to thermodynamics.)

Thus the important fact is established that free atoms (and also radicals) can recombine only in a triple collision. The probability of recombination is about proportional to the pressure of the gases present (although individual differences are experienced). This has been observed not only in the case of bromine but also in the reactions of atomic hydrogen. To be sure, the case can be different in the recombination of multiatomic radicals, just as the energy for activation in monomolecular disintegrations can amount to many degrees of freedom. It is therefore conceivable that the reaction energy also in the case of recombination is distributed over many degrees of freedom in the same molecule and that the life span of the molecule formed becomes so great that it exceeds the average time between two impacts and that therefore practically every new-formed molecule is deactivated by impact, and the reaction takes its course in a double collision.<sup>2</sup>

The last fact of general importance, which we shall meet in the photochemical HBr formation, is the destruction of bromine atoms on the wall (this process, too, is not noticeable in thermal reaction where for thermodynamic reasons just as many Br-atoms must be formed at the wall as must be destroyed). Experimentally it is found that the velocity of the photochemical HBr formation falls below the expected values, if either the container dimensions are reduced or the pressure is greatly reduced. Both effects can be explained qualitatively and, as far as a computation is possible, also quantitatively by the fact that bromine atoms, except in the gas phase, can also be destroyed by recombination in the triple collision at the wall, perhaps in such a way that a bromine atom striking the wall remains absorbed there till a second atom joins it and recombines with it. We shall not offer a treatment of the important diffusion phenomena (cf. Jost and Jung<sup>1</sup>); we wish only to point to the fact that in this and other static chain reactions, wall influences of this kind are

<sup>1</sup> JOST, W., and G. JUNG, *Z. physik. Chem., Sec. B*, **3**, 83 (1929). JOST, W., *Z. physik. Chem., Sec. B*, **3**, 95 (1929). HILFERDING, K., and W. STEINER, *Z. physik. Chem., Sec. B*, **30**, 399 (1935). RABINOWITSCH, E., *Z. physik. Chem., Sec. B*, **33**, 275 (1936). RABINOWITSCH and LEHMANN, *Trans. Faraday Soc.*, **31**, 689 (1935). RABINOWITSCH and W.C. WOOD, *Trans. Faraday Soc.*, **32**, 907 (1936). RABINOWITSCH, *Trans. Faraday Soc.*, **33**, 283 (1937). RABINOWITSCH and WOOD, *J. Chem. Phys.*, **4**, 497 (1936).

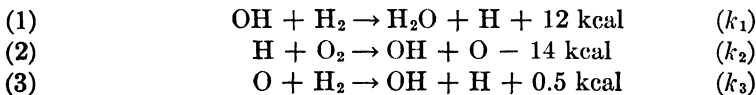
<sup>2</sup> KIMBALL, G., *J. Chem. Phys.*, **5**, 1937. KASSEL, L.S., *J. Chem. Phys.*, **5**, 992 (1937).



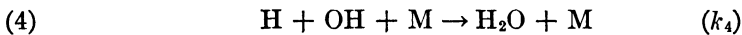
known and explainable. In the discussion of nonstatic chain reactions, we shall find it necessary to discuss them in greater detail.

The temperature dependence in compound reactions can frequently be expressed by an exponential function  $e^{-Q/RT}$ , where  $Q$ , however, need not always have a simple meaning as activation heat. By the overlapping of several reactions, various conversion mechanisms can sometimes predominate in various temperature ranges, and thus various temperature dependencies can result. In such cases, and in reactions with chain-branching, in which the reaction velocity over a limited temperature interval changes as  $\exp(-Q/RT)$  changes and in which this formula has more the character of an interpolation formula, we designate  $Q$  as "apparent activation heat." In such cases, the factor appearing in addition to the  $e$  power is of a different order of magnitude from what we should ordinarily expect.

**4. Reactions with Chain-branching.**—An important class of reactions that it is still necessary to discuss is that of "chain-branching." We cannot take any simple thoroughly investigated example, however, for the simplest combustion reaction of this type, the oxygen-hydrogen combustion, is not so clear as the more simple chain reactions of the hydrogen halides. Of oxygen-hydrogen combustion, this much is known with certainty (see Chap. IX), that at higher temperatures it occurs with free atoms and radicals and that in addition to H-atoms the radical OH takes part, which has also been shown to be present in thermal equilibrium at higher temperatures (above 1000°) by Bonhoeffer and Reichard.<sup>1</sup> If we attempt to formulate a reaction mechanism with it (*cf.* Chap. IX), we should arrive at something like the following reactions (for the chain induction, we do not want to make any definite assumptions):



and as chain-breaking,<sup>2</sup> perhaps among others,



This pattern again represents a chain reaction. (1), (2), and (3) are chain-continuing reactions. After (4) and similar reactions, there is a chain break.<sup>2</sup> As opposed to the chain reactions discussed previously, here something new is added. In the reactions, steps (2) and (3), there appears on the right side for each active particle entering the reaction (H- or O-atom) not only one new active particle but two, one OH-radical + one H-atom. If the number of the new active

<sup>1</sup> BONHOEFFER, K.F., and REICHARD, *Z. physik. Chem.*, Sec. A, **139**, 75 (1928).

<sup>2</sup> Other reactions will actually predominate in chain-breaking.

particles arising according to (2) and (3) is greater than those disappearing according to (4) and analogous equations, their number and therefore the reaction velocity in the course of conversion must increase constantly, *i.e.*, an explosion must take place even under conditions under which the reaction mixture does not spontaneously heat up. Explosions of that kind have frequently been observed under low pressures, and the concept of reaction chains was developed by Semenov to explain them. At this point, we shall leave open the question of the nature of the mechanism involved in oxygen-hydrogen mixtures. At higher temperatures, chain members as we have described them certainly play a role, although, to be sure, with a different breaking reaction.

Obviously the nature of the chain-inducing reaction does not need to play a role in the appearance of an explosion if active centers are formed at all. It depends only on whether the reactions leading to an increase of the active centers [(2) and (3) in our example] are compensated for by the reactions combining active centers [like (4)] or not.

If we attempt to compute the static reaction velocity of the hydrogen combustion given above, as we have done for the HBr formation, the following method is used: We again assume that the concentration of the active particles is static, *i.e.*, the corresponding differential quotients at time = 0. We do not introduce a special chain-inducing reaction. The number of the active particles must, of course, increase if we have introduced even a few such particles at the beginning. Then

$$\begin{aligned} \text{(I)} \quad & d[\text{H}]/dt = k_1[\text{OH}][\text{H}_2] - k_2[\text{H}][\text{O}_2] + k_3[\text{O}][\text{H}_2] - k_4[\text{H}][\text{OH}][\text{M}] \\ \text{(II)} \quad & d[\text{O}]/dt = k_2[\text{H}][\text{O}_2] - k_3[\text{O}][\text{H}_2] \\ \text{(III)} \quad & d[\text{OH}]/dt = -k_1[\text{OH}][\text{H}_2] + k_2[\text{H}][\text{O}_2] + k_3[\text{O}][\text{H}_2] - k_4[\text{H}][\text{OH}][\text{M}] \end{aligned}$$

From (II)

$$[\text{O}] = \frac{k_2[\text{H}][\text{O}_2]}{k_3[\text{H}_2]}$$

Eqs. (I) to (III) yield

$$2k_1[\text{OH}][\text{H}_2] - 2k_2[\text{H}][\text{O}_2] = 0$$

or

$$[\text{OH}] = \frac{k_2[\text{H}][\text{O}_2]}{k_1[\text{H}_2]}$$

Insertion of the expressions for [O] and [OH] in (I) gives

$$[\text{H}] = \frac{k_1[\text{H}_2]}{k_4[\text{M}]}$$

and thus

$$[\text{O}] = \frac{k_1 k_2 [\text{H}_2][\text{O}_2]}{k_3 k_4 [\text{H}_2] \text{M}} = \frac{k_1 k_2 [\text{O}_2]}{k_3 k_4 [\text{M}]}, \quad [\text{OH}] = \frac{k_2 [\text{O}_2]}{k_4 [\text{M}]}$$

For the velocity of water formation, we then find

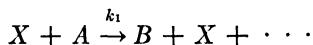
$$\frac{d[\text{H}_2\text{O}]}{dt} = \frac{2k_1 k_2 [\text{H}_2][\text{O}_2]}{k_4 [\text{M}]}$$

We thus obtain an expression that is in no way different externally from expressions valid for static reactions and that would thus suggest that we are dealing with a static

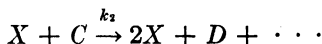
reaction in this case too. If, however, we were to put the numerical values of the individual constants into the equation and thus anticipate experimental results, which we shall discuss later, we should find that, according to this mechanism, the reaction at 450°C would practically have come to an end after a fraction of a second, in other words, that an explosion would have taken place. If we likewise computed the "static" concentration of the [H] atoms according to the above equation, we should obtain a value that is higher than the [II<sub>2</sub>] concentration usually applied; i.e., explosion has again occurred by chain-branching. In addition, it naturally follows that the concentrations of the intermediate products like [H], etc., at least at high temperatures, are by no means static under reasonable conditions and that therefore the entire manner of computation given above cannot any longer be applied, making it necessary to substitute another.

We could conclude from the above pattern—and this has often been done—that in chain-breaking according to the second order [reaction (4)] and in chain-branching only according to the first order [reactions (2) and (3)], the breaking of the branching would finally always have to compensate for a sufficiently high concentration of the active particles and that therefore no explosion could occur. As can be seen, however, such an argument loses its force if a compensation would appear only at such a high concentration of the active particles that the reaction would practically have come to an end previously with a velocity that would mean explosion. Of course, it must be borne in mind that the above equations do not suffice to describe the processes actually observed in oxygen-hydrogen explosion.<sup>1</sup>

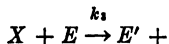
In order to derive the relations for chain explosions in the usual form, as first discussed by Semenov, we shall consider the simplest possible pattern of the reaction with chain-branching. A substance *A* is to change to a substance *B* by reaction with active particles *X* with regeneration of the particles *X* and the formation of other possible inactive particles



(In actual examples, perhaps a second active particle *Y* is produced in the same phase of the reaction that regenerates the particle *X* only after reaction with *A* or with another substance; but this does not change anything essential in the above simple case.) Let chain-branching appear by reaction of *X* with the type of molecule *C*, for example,



while the active particles disappear, and chains are thus broken, perhaps according to



<sup>1</sup> Cf. Chap. IX.

If we attempted to compute the static velocity from this according to our usual method, we should get

$$\frac{d[X]}{dt} = k_2[X][C] - k_3[X][E] = 0$$

and from this

$$k_2[C] = k_3[E] \quad (50)$$

We thus obtain no value at all for the static concentration of  $[X]$  but rather a condition between two velocity constants and two concentrations. If this condition is fulfilled, the reaction velocity becomes static for any value of  $[X]$ . The concentration of  $X$  and the reaction velocity therefore remain undetermined. If the expression for  $d[X]/dt$  is positive, however, that is,  $k_2[C]k_3[E]$ , the concentration  $[X]$ , and therefore the reaction velocity, constantly rises, and the condition (50) therefore characterizes the borderline case for the chain explosion. A condition of the form (50) results for chain explosions in general, according to Semenov.<sup>1</sup> As long as we are far enough removed from the limits of explosion and have a static reaction velocity, it is necessary to take into account another chain-inducing reaction producing particles like



for example, let  $X$  be formed by dissociation of  $U$  or according to any other process of the first order from  $U$ ; then the following is valid:

$$\frac{d[X]}{dt} = k_0[U] + k_2[X][C] - k_3[X][E] = 0; \quad [X] = \frac{k_0[U]}{k_3[E] - k_2[C]}$$

Thus the reaction velocity  $w$  becomes

$$w = \frac{d[B]}{dt} = k_1[X][A] = \frac{k_1k_0[A][U]}{k_3[E] - k_2[C]} \quad (51)$$

The reaction velocity thus has a definite value as long as the denominator is positive. If the denominator is zero, it means that the process is passing over into explosion and leads again to condition (50)

$$k_3[E] - k_2[C] = 0$$

as a borderline condition for a chain explosion.

We wish to change the above equation for  $w$  somewhat in order to adapt it to the form that has become customary since Semenov. By the chain-inducing reaction, active centers  $X$  appear in the time unit  $k_0[U]$ . An active center reacts  $k_1[A]$  times with molecules  $A$ . Therefore, the number of the primary reactions in the time unit,  $n_0$ , is proportional to  $k_0k_1[A][U]$ . The expression  $k_3[E]$  is proportional to the probability that a particle  $X$  is destroyed and the chain broken. We shall designate this expression with  $\beta$ . Correspondingly,  $k_2[C]$  is proportional to the probability that an additional particle  $X$  is formed and the chain is branched. We shall designate this probability with  $\delta$ . Thus the expression for the

<sup>1</sup> Cf. the criticism on pp. 279ff.

reaction velocity<sup>1</sup> becomes

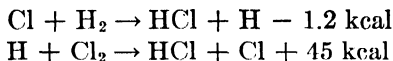
$$w = \frac{n_0}{\beta - \delta}$$

If we disregard a proportionality factor, we can designate  $\beta - \delta$  as the resulting probability for the chain break. The reaction velocity is finite only as long as this probability possesses a positive value. The condition for explosion is chain-break probability = chain-branching probability,

$$\beta = \delta$$

We have always assumed free atoms and radicals to be active particles, and thus we have limited ourselves to the special case of "material chains." This is not necessary. In the case of "energy chains," the above relations of chain explosion are also valid. Indeed, the transfer of liberated reaction energy that leads to chain-branching was originally the point of departure of Semenov's findings. We speak of energy chains if energy-rich activated particles, stable in themselves, are responsible for the continuation of the reaction, like molecules with a certain minimum energy  $\epsilon$ , whose fraction in the thermal equilibrium is  $e^{-\epsilon/kT}$ . It was formerly customary to introduce such particles as chain reactions, but since the deactivation probability of stimulated particles in impacts is very high, the cases are probably rare in which such active particles appear in a concentration much higher than that corresponding to the thermal equilibrium.

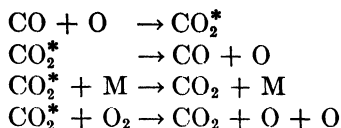
However, a mixed energy-material chain, as Semenov has proposed for the explanation of the chain explosion for chlorine-hydrogen gas and for many other cases, may often appear



In the second reaction, the reaction heat will be able to distribute itself to the reaction products in various ways. In any case, stimulated  $\text{HCl}^*$  molecules will arise that can have an energy content up to 45 kcal in the form of rotation and oscillation heat. If such an  $\text{HCl}^*$ -molecule collides with a  $\text{Cl}_2$ -molecule, which has a minimum energy content of (dissociation heat - energy of the  $\text{HCl}^*$ -molecule), the dissociation of the  $\text{Cl}_2$ -molecule and hence chain-branching is possible. Such processes of

<sup>1</sup> Since in general at least  $n_0$  and  $\delta$  will vary exponentially with the temperature, the resulting temperature dependence is rather complicated. Especially, if  $\delta$  is only a little smaller than  $\beta$ , the velocity can vary to an extraordinarily great degree with the temperature. If we represent the velocity over a limited range of temperature formally by  $\exp(-Q/RT)$ , the "apparent heat of activation  $Q$ " can assume uncommonly high values.

energy transfer may perhaps play a role in CO combustion,<sup>1</sup> where, in the absence of water vapor, a mechanism of explosion of the following type is plausible:



Here the oxygen atoms are assumed to be the active particles. The formation of  $\text{CO}_2$  from  $\text{CO} + \text{O}$  in a triple collision is divided into two steps, merely formal, namely, in the formation of an energy-rich complex  $\text{CO}_2^*$ , which can either disintegrate spontaneously into  $\text{CO} + \text{O}$  or be stabilized in a triple collision with any molecule M that absorbs the excess energy. If this triple collision partner is an oxygen molecule, the energy absorbed from  $\text{CO}_2^*$  can lead to the dissociation of  $\text{O}_2$  and hence to chain-branching.

The borderline condition for chain explosion

$$\beta - \delta = 0$$

has demonstrated its value especially in the explanation of the critical explosion pressure limits. As we have already mentioned, explosion ranges of the kind shown in Fig. 158 are frequently observed at lower pressures. In Fig. 158, the shaded range corresponds to that of chain explosion. Below limit I and above limit II, no explosion appears; or, differently expressed, under the special conditions, the ignition temperature, beginning at very low pressures, at first drops with increasing pressure but then rises again and finally goes over into a relation (dashed line) that can express a heat explosion (but not necessarily). A limit like I can obviously be explained in the following manner: If the chain-branching is either independent of the pressure or increases with increasing pressure, while the chain-breaking is inversely proportional to the pressure, in other words, takes place at the wall and is determined by the velocity of the diffusion of the chain agent to the wall, the breaking probability must (below a certain pressure) outweigh the branching probability, and a limit corresponding to I must be established. That this explanation of the "lower" explosion limit is probably generally applicable is substantiated by many findings. If this is true, definite

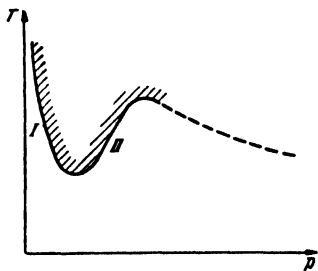


FIG. 158.—Explosion limits in chain explosion.

<sup>1</sup> Cf. Chap. IX.

dependencies on the dimensions of the container must result. The greater the diameter of the container, the smaller the velocity of the diffusion to the wall; hence also the lower the explosion limit, a fact that is verified again and again. Further, the diffusion velocity of inert foreign gases is influenced to the same extent as that of the gases taking part in the reaction. The addition of inert foreign gas can therefore aid explosion. Both facts are corroborated by experience. In general, the position of the lower explosion limit cannot readily be reproduced, and this too fits the facts, for the chain break at the wall is dependent to a sensitive degree on the momentary condition of the wall. In borderline cases, remarkable relations exist, as we shall see below.

An upper explosion limit, the nonappearance of an explosion with increased pressure, is obviously possible only when the deactivation, *i.e.*, the destruction of the chain agents, rises with a higher power of the pressure than the new formation of chain agents by chain-branching. We can therefore be dealing only with processes in the gas phase in which, for example, the chain-branching is a reaction of the second order but the chain break is a triple collision reaction. The interpretation of the upper limit is not always easy in detail. The fact that it can easily be produced is characteristic for the upper limit, as well as the fact that its position is in general independent of the wall material (an important assumption; *cf.* Chap. IX, page 310), a proof that deactivation in the gas phase must actually be responsible for the appearance of this pressure limit.

It will be necessary to regard the chain-heat explosion as a more general type of explosion. Even though few systematic experiments have been made, it is nevertheless likely that this case is realized especially under technically important conditions of explosion at high initial pressure. Without chain-branching, the reaction velocity could not grow to considerable values in very short times. On the other hand, the conditions for heat conduction at somewhat higher pressures are of such a nature that, as soon as the reaction velocity has noticeably increased, a practically complete conduction of the reaction heat can no longer come into consideration.

Before continuing with the discussion, we shall attempt to formulate quantitatively the relations developed above. In this, we shall follow Semenov.<sup>1</sup>

For this purpose, we shall consider first of all the reaction with the chain break at the wall. We shall from the first disregard branching entirely and compute only the static velocity. For simplicity, we shall assume an infinitely extended container bordered by plane-parallel walls at a distance of  $2d$ , because the diffusion relations are especially simple in this case. It would occasion no great difficulties if a cylindrical or

<sup>1</sup> SEMENOFF, N., "Chemical Kinetics and Chain Reactions," Oxford, 1935.

spherical container were treated exactly. In general, however, it does not pay to go beyond the computation of the simple case assumed above, for the following reasons. We shall take into consideration only pure diffusion; but practically, except at very low pressures, convection will also play a role. Convection can be introduced only by an empirical correction factor, however. The solution of the problem also requires definite assumptions on the condition of the wall. It must be assumed either that every active particle striking the wall is destroyed (which is quite true in some cases) or (which the experiments corroborate in other cases) that only the fraction  $\epsilon$  of all the impacts of active particles against the wall leads to chain-breaking, in which  $\epsilon$  sometimes can be very small,  $10^{-4}$  or below. It is clear that  $\epsilon$  is greatly dependent on the condition of the wall; it can change from experiment to experiment in the same reaction container or even in the course of a single experiment, and this can make exact quantitative results extraordinarily difficult to obtain. If, however, the indefiniteness of the yield factor in chain-breaking introduces essential uncertainties into the result, an overexact treatment of the diffusion problem (which, in addition, would change little in the form of the solutions obtained) would hardly be justified. If we put the  $x$ -axis of a coordinate system perpendicular to the bordering parallels of our reaction container and if we allow the zero point to fall midway between the plates (Fig. 159), the following differential equation for the static concentration of active particles would result if we designate the number of active particles per  $\text{cm}^3$  spontaneously formed in the unit of time with  $n_0$ :

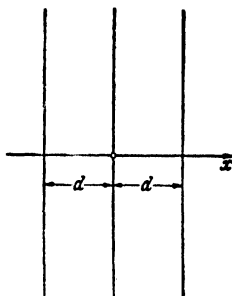


FIG. 159.

$$n_0 + D \frac{d^2 n}{dx^2} = 0 \quad (52)$$

in which the second member represents the decrease in concentration of active particles by diffusion<sup>1</sup> to the wall and  $D$  represents the diffusion [coefficient of these particles in the gas mixture in question.

Equation (52) can be integrated and yields

$$\frac{dn}{dx} = -\frac{n_0}{D} x + C; \quad n = -\frac{n_0 x^2}{2D} + C_1$$

[a member with  $x$  may not appear,  $C$  must = 0, since the concentration distribution is symmetrical to the middle plane of the plates,  $\left(\frac{dn}{dx}\right)_{x=0} = 0$ ]. If we now place

<sup>1</sup> Cf. Frank-Mises (quoted p. 49) and the expressions used elsewhere, *e.g.*, Chap. III, p. 117.



the yield of impacts at the wall at  $\epsilon = 1$ , in other words, assume that every active particle striking the wall is destroyed there, then also  $n = 0$  at the wall (*i.e.*, for  $x = \pm d$ ), and thus

$$n = \frac{n_0}{2D} (d^2 - x^2) \quad (53)$$

The concentration of active particles is now naturally spatially variable, with a maximum in the middle of the container. For the gross reaction velocity to be observed, we are interested in the average concentration  $\bar{n}$  in the reaction container for which the following is obtained by integration:

$$\bar{n} = \frac{1}{2d} \int_{-d}^{+d} n \, dx = \frac{n_0}{4dD} \left[ d^2(d+d) - \left( \frac{d^3}{3} + \frac{d^3}{3} \right) \right] = \frac{n_0 d^2}{3D} \quad (54)$$

That is, the number of active centers, and therefore also the reaction velocity, is proportional to the square of the container width and inversely proportional to the diffusion coefficient. Since the latter is inversely proportional to the pressure, the composition remaining constant,

$$D = \frac{\text{const}}{p}$$

one obtains for  $n$

$$n \sim d^2 p \quad (55)$$

That is,  $n$  and the reaction velocity are proportional to the total pressure, although, to be sure, only as long as  $n_0$  is independent of the pressure. If the gas mixture is composed of the components 1, 2, . . . with the partial pressures  $p_1, p_2, \dots$  then

$$D \cong \frac{\text{const}}{k_1 p_1 + k_2 p_2 + \dots}$$

in which the individual  $k_1, k_2, \dots$  take care of the various impact cross sections of the individual gases. Thus  $n$  becomes

$$n \sim d^2 (k_1 p_1 + k_2 p_2 + \dots)$$

Relations of this form are frequently found fulfilled at the wall for the velocity of chain reactions with chain-breaking.

However, it is easy to see—although this fact has been clearly recognized only relatively recently—that, with chain-breaking at the wall, relations can also be obtained into which the coefficients do not enter and the dimensions of the container enter only indirectly. If, namely,  $\epsilon$ , the breaking probability in an impact against the wall, is very small, the diffusion velocity in breaking at the wall will play no role in the velocity of the chain break; for now only a very small decrease in the concentration of the active particles to the wall will appear. Even this small decrease in practically constant spatial concentration suffices, however, to move as many active particles to the wall as are destroyed there in the

fraction  $\epsilon$  of all gas-kinetic impacts against the wall. If  $O$  is the total surface of the container and  $\bar{w}$  the average molecular velocity, then in the unit of time  $\frac{n\bar{w}O\epsilon}{4}$  such impacts take place (cf. page 251) if  $n$  is the static concentration of active particles. The number of the active particles spontaneously formed in the entire volume  $V$  in the unit of time is  $n_0V$ . Since in a static condition just as many particles are formed as disappear, the following is valid:

$$\frac{n\bar{w}O\epsilon}{4} = n_0V$$

or

$$n = \frac{4n_0V}{\bar{w}O\epsilon}$$

In our case,  $V = Od$ ; in this indirect way, the dimension of the container enters the final equation from which  $D$  and thus  $p$ , however, have completely disappeared

$$n = \frac{4n_0d}{\bar{w}\epsilon} \quad (56)$$

Therefore, in this case also, the greater the dimensions of the container, the greater the static concentration of active particles, and therefore the reaction velocity is proportional only to the first power (cf. page 276).

If instead of the form of the container chosen by us, a different one had been taken, let us say, a sphere, only the numerical factor entering into (56) would have been changed somewhat. This result is important, especially for qualitative considerations. The dependency of the reaction velocity and therefore also of the explosion limit on the pressure demanded according to (54) and (55) has always been regarded as a decisive criterion for chain-breaking at the wall, but these observations show that this need not necessarily be the case. Even the dependence on the square of the container width can be removed, and chain-breaking at the wall will nevertheless be determining.

We could treat the two borderline cases  $\epsilon \cong 1$  and  $\epsilon \ll 1$  in a simplified manner and obtain the result even in its most important quantitative respects without difficult computation. The intermediate range, which of course represents the majority, requires more careful consideration. It is possible to give the solutions for it too, but we shall dispense with them here, since we shall make no use of the quantitative relations for them. We therefore simply refer to Lewis and v. Elbe.<sup>1</sup> We are here chiefly concerned with showing how varied the relations in the case of

<sup>1</sup> LEWIS, B., and G. v. ELBE, *J. Am. Chem. Soc.*, **75**, 970 (1935); also "Combustion, Flames and Explosions of Gases." KASSEL, L.S., and STORCH, *J. Am. Chem. Soc.*, **57**, 672 (1935).

chain-breaking at the wall can be and how necessary it is to be careful in interpreting the results if errors are to be avoided.

We shall now introduce chain-branching and investigate the explosion conditions for the above relations. We shall have to add to the above expressions that of chain-branching. If we assume the chain-branching to be proportional to  $n$  and the number of the active centers to  $fn$ , then the number of the active particles formed in the unit of time per  $\text{cm}^3$  is

$$n_0 + fn$$

and the particles destroyed by diffusion on the wall again is  $\frac{D}{dx^2} \frac{d^2n}{dx^2}$  (for the infinitely extended container bounded by two plane plates perpendicular to the  $x$ -axis). In the static condition, therefore, the following is valid:

$$D \frac{d^2n}{dx^2} + fn + n_0 = 0 \quad (57)$$

Equations of this kind have been treated by Bursian and Sorokin

In order to realize how the explosion limit comes about, we can proceed in the following manner: In the breaking probability 1 per impact on the wall, we obtained for the static concentration of the chain agents

$$n \sim \frac{n_0 d^2}{D}$$

that is, up to 1, the breaking velocity is proportional to  $nD/d^2$ . For purposes of approximation, we may simply adopt this expression for chain-branching. The resulting breaking probability is obtained by subtraction of the branching probability from the breaking probability to<sup>2</sup>

$$k \frac{nD}{d^2} - fn$$

and thus the static concentration of active particles and the reaction velocity is proportional to

$$n \sim \frac{n_0}{k(nD/d^2) - fn} \quad (58)$$

where  $k$  is still a numerical factor whose value is determined by more exact computation. The explosion condition then is

$$\frac{kD}{d^2} - f = 0 \quad (58a)$$

However, if we again consider that the diffusion coefficient is inversely proportional to the total pressure  $p$ , or, more exactly, inversely proportional<sup>3</sup> to  $\sum k_i p_i$ , and that the branching probability  $f$  will be proportional

<sup>1</sup> BURSIAK and SOROKIN, *Z. physik. Chem.*, Sec. B, **12**, 247 (1931). Cf. also SEMENOFF, "Chemical Kinetics and Chain Reactions."

<sup>2</sup>  $k$  is a proportionality factor.

<sup>3</sup>  $p_i$  represents the partial pressures of the individual components.

to a Boltzmann factor  $e^{-E/RT}$ , then we arrive from (58a) at the following expression

$$d^2 p e^{-E/RT} = \text{const} \quad (59)$$

where, for more exact computations,  $\Sigma k_i p_i$  would appear in place of  $p$ . It follows from this that, at constant temperature, the critical explosion pressure would be inversely proportional to the square of the container width, a relation that could frequently be corroborated (*cf.* pages 283ff.), and further that the critical explosion pressure like  $e^{+E/RT}$  drops with increased temperature. This is formally the same relation that we have derived for thermal explosion. In (59), the first power of  $p$  appears only if the branching probability  $f$  is independent of the pressure; if the latter were proportional to  $p$ , then instead of (59) the following would be valid:

$$d^2 p^2 e^{-E/RT} = \text{const}$$

As a matter of principle, the following should be pointed out: Under the above assumption that chain-breaking takes place at the wall and the diffusion of the chain agents against the wall is determining for the velocity, the breaking probability is always proportional to  $p^{-1}$ . Insofar as the branching probability is independent of the pressure or proportional to a power of the pressure higher than the  $(-1)$ st, a critical pressure limit always results above which explosion again occurs. If in addition there is a chain-breaking process in the gas phase that is proportional to a still higher power of the pressure, then there must also be an upper explosion limit above which explosion is again impossible. One presupposition for the appearance of the limits, in a form given by Semenoff, is that the chain-breaking and chain-branching reaction is of the same order in respect to the concentrations of the active particles, for the explosion condition no longer contains their concentration (*cf.*, however, pages 279ff.).

All the relations, however, are now complicated by the fact that, as we have already discussed, the probability of chain-breaking in the case of an impact against the wall,  $\epsilon$ , can be very small. Then the dependence on the dimensions of the container and on pressure in the form of (59) can be disregarded (*cf.* in this connection Lewis and v. Elbe, quoted page 273). To this must be added a complication not yet mentioned, namely, that the wall can be not only negatively but also positively catalytic, *i.e.*, chains can proceed from it. Therefore all combinations with chain induction in the gas phase and at the wall, with chain-breaking in the gas phase and at the wall, and finally also with chain-branching in the gas phase and at the wall are to be taken into account. We do not wish to concern ourselves unnecessarily with formal considerations, however, and shall therefore mention only the case of chain induction and chain-

breaking at the wall. This case is treated by Semenoff and by Lewis and v. Elbe (quoted page 273). In this case too, the reaction velocity—unlike what we might expect—is still dependent on the diameter of the container, but only on its first power, as long as  $\epsilon$  is not  $\ll 1$  (cf. Lewis and v. Elbe, quoted page 273).

If  $\epsilon \ll 1$  and the breaking velocity is (cf. page 273) given by  $n\bar{w}O\epsilon/4$ , the following results for the static condition. If  $m_0$  chains are induced per unit of wall surface, it must be equal to the above expression, in other words,

$$n = \frac{4m_0}{\epsilon\bar{w}}$$

The reaction velocity is thus completely independent of the dimensions of the container.

We shall not develop in detail the theory of the upper explosion limit, since we shall become acquainted with it later by examples (pages 283ff.). Here we shall only mention the fact that, if the branching velocity is a certain function of the pressure (or the partial pressures), let us say,  $\sim p^n$ , and if there is a chain-breaking in the gas phase that is proportional to a power  $m > n$  of  $p$ , then with increasing pressure a limit must eventually be reached at which the breaking in the gas phase compensates for the branching, and the explosive reaction therefore again slows down. By the cooperation of chain-breaking at the wall, which is favored by low pressure and a mechanism in the gas phase about the nature of which no general predictions can be made but about which it must be assumed that it is favored by rising pressure (like a triple collision reaction), the island-like form of the explosion region comes about (Fig. 158). It has already been shown that the branch of the lower explosion limit (up to the neighborhood of the minimum) can be expressed by an exponential formula. Under the presuppositions mentioned, this is also true of the branch II of the upper explosion limit; for, if the branching is proportional to  $e^{-E/RT}$ , the breaking proportional to the pressure (in the above relation,  $m = 1, n = 0$ ), the following is true for stationarity:

$$kp = e^{-E/RT}$$

that is, the pressure rises at the upper explosion limit (or a power of the pressure) exponentially with the temperature just as the pressure (in general at a power different from that at the upper limit) decreases exponentially at the lower level. A third limit (dashed line in Fig. 158) that often appears could be explained on the basis of the chain theory, but it appears to us much more probable that we are here dealing rather with the presuppositions of thermal explosion, even though it might be a matter of chain reaction with branching.

If we write the reaction velocity according to Semenov in the form

$$w = \frac{k}{\beta - \delta}$$

the explosion limits are indicated by the positions  $\beta - \delta = 0$ . If  $\beta - \delta$  is plotted as a function of the pressure, for constant temperature, the zero positions correspond to infinity positions of the reaction velocity, in other words, explosion limits (Fig. 160). Also, the course of the reaction velocity is given in the figure by the dashed lines. It presents no difficulty, of course, to think of the function  $\beta - \delta$  as approximated polynomially in powers of the pressure, necessitating our beginning generally with the  $(-1)$ st power. The higher the powers of the pressure we take into account, the more zero positions are obtained; but it is hardly feasible physically to go beyond two zero positions corresponding to the upper and lower explosion limits.

In the discussion so far, we have been dealing with stable types of molecules in the case of the pressure or the reaction order and not with active particles. In respect to the latter, it was generally tacitly assumed that the reaction was of the first order. In chain-breaking at the wall and in velocity-determining diffusion, this is, for example, always the case. Chain-branching according to a mechanism, like  $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$ , is likewise of the first order in respect to the active particle H. Chain-breaking in the gas phase, *e.g.*, by reaction of an active particle with a foreign substance that is present as a minor impurity, would likewise be of the first order in respect to the active particles (*e.g.*, a reaction  $\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2$ ). Actually, Semenov's formal relations are valid only for reactions into which the active particles enter with the first order (in themselves, they would also be valid for higher orders but only if the active particles entered in breaking and branching reactions with exactly the same higher orders, a thing that can generally be excluded as too improbable); for an explosion condition independent of the concentration of the active particles can be obtained only if the breaking probability  $\beta$  and the branching probability  $\delta$  are each given by

$$\beta = gn \quad \text{and} \quad \delta = fn$$

It then follows from the explosion condition

$$\beta - \delta = 0 \quad g - f = 0$$

(w)

w

$\beta - \delta$

FIG. 160.—Resulting breaking probability,  $\beta - \delta$ , and reaction velocity  $w$  as functions of the pressure in a reaction with chain-branching.

independent of  $n$ . If a member quadratic in  $n$  occurred in the breaking probability (originating from the recombination of two active particles in the gas phase), we should obtain, as has already been mentioned (*cf.* pages 265, 275)

$$\beta - \delta = g_0 n + g_1 n^2 - f n \quad (60)$$

This expression never becomes zero for sufficiently high values of  $n$ , that is, we shall formally never obtain explosion, but rather a static reaction. It would not be permissible to conclude, however, that the reaction would necessarily have to be static; it depends rather on the numerical values of the individual reaction velocities. If the total velocity, as in the example treated at the beginning (page 264), is so high that everything has reacted in a few seconds or in a fraction of a second, there is explosion, even though the formal expression obtained does not fit the simplified pattern, according to Semenov.

As a matter of principle, the following must be determined for the explosion condition: The reaction velocity becoming infinite is nothing but a convenient mathematical formulation for "becoming very great." In finite quantities of material to be converted, the reaction velocity can actually never become  $\infty$ , because the consumption of the initial substances prevents it. In general, however, this mathematical simplification is useful and produces correct results. If in special cases the formal computation leads not to an infinite but rather to a very great reaction velocity, it would be hasty to assume that the contradiction to the simplified mathematical formulation would mean that no explosion is present. Rather, the experimental result is only a very great reaction velocity, and this can also be the result of the computation.

Moreover, this case, too, is of importance, and perhaps of greater importance than would seem to be suggested by the examples investigated up to now, namely, that the reaction is really not accelerated up to the point of explosion by chain-branching but that it has been accelerated up to the point at which the heat equilibrium has been disturbed and a thermal explosion finally takes place as a result of a reaction at first accelerated by chain-branching.<sup>1</sup>

At this point, we shall also mention the case that Semenov designates as reciprocal chain action, that chain-branching also appears in a reaction of the second order in respect to the active particles. Therefore

$$\frac{dn}{dt} = n_0 + f'n^2 - gn \quad (61)$$

<sup>1</sup> *Cf.* NORRISH, R.G.W., quoted pp. 417.

if  $n$  is to be static, then it follows from this (with  $dn/dt = 0$ )

$$n = \frac{g - \sqrt{g^2 - f'4n_0}}{2f} \quad (62)$$

The solution is imaginary, *i.e.*, the stationarity is lost and explosion appears if

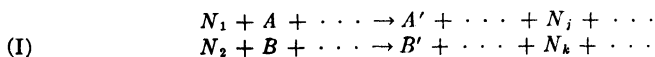
$$4f'n_0 \geq g^2 \quad (63)$$

That means, however, that here, in contrast to the cases considered earlier, the appearance of the explosion is favored by an increase in the number of the initial centers. The result is not entirely unexpected, but it must be emphasized that, without the introduction of the quadratic member, such an effect, according to a strict chain theory, could not appear. However, we must again call the following to mind: Even without reciprocal chain action, the *static* velocity is proportional to the number of spontaneously formed initial centers

$$w \sim \frac{n_0}{\beta - \delta}$$

If this static velocity is, to be sure, measurable but small, and the concentration of the initial centers is increased artificially (in materials that disintegrate into active particles by light absorption, *e.g.*, chlorine molecules in chlorine detonating gas by means of lighting) by a number of powers of 10, then the reaction velocity too would increase several powers of 10, and this could suffice to render it explosive or at least to lead to the induction of a thermal explosion. At any rate, it can be seen that promoting explosion by means of increasing the number of the initial centers need not necessarily be conditioned by reciprocal chain action. It is possible that we need not introduce it at all.

It can be shown<sup>1</sup> that, even by assuming only such elementary reactions as are of the first order in respect to the active particles, an expression is obtained as an explosion condition that cannot always be reduced to Semenov's condition  $\beta - \delta = 0$ , with  $\beta$  proportional to the breaking probability and  $\delta$  proportional to the branching probability. If we disregard the chain-inducing reactions (which is permitted as long as the production of active centers by the primary reaction is negligibly small in proportion to the production by chain-branching) and if we assume as chain-continuing, chain-branching, and chain-breaking reactions only those which are of the first order in respect to the various active particles  $N_i$ , we can write the following pattern of reactions:



<sup>1</sup> Jost, W., and L. v. MÜFFLING, *Z. physik. Chem., Sec. A*, **183**, 43 (1938).



in which  $A, B, A', B' \dots$  are to be stable types of molecule. In each equation of this pattern, an active particle appears to the left; and to the right, 0, 1, or 2 particles can appear according to whether we are dealing with a chain-breaking, chain-continuing, or chain-branching reaction. From the pattern I, we obtain for the temporal change of the concentration  $n_i$  of the individual active particles, the following system of differential equations:

$$(II) \quad \begin{aligned} \frac{dn_1}{dt} &= a_{11}n_1 + a_{12}n_2 + \dots \\ \frac{dn_2}{dt} &= a_{21}n_1 + a_{22}n_2 + \dots \\ &\dots \dots \dots \end{aligned}$$

The individual coefficients  $a_{jk}$  have the form

$$a_{jk} = \pm k_a[A'']^{j-1}[A'''] \pm k_\beta[B'']^{j-1}[B'''] \pm \dots$$

that is, they depend on the concentration of stable molecules  $A'' \dots B'' \dots$ , etc., and the various velocity coefficients but not on the concentrations of active particles. In a nonstatic reaction, it would be necessary to integrate the system (II) of simultaneous differential equations. If we assume with Bodenstein the disappearance of the  $dn_i/dt$  as a condition for stationarity, it follows:

$$(III) \quad \begin{aligned} a_{11}n_1 + a_{12}n_2 + \dots &= 0 \\ a_{21}n_1 + a_{22}n_2 + \dots &= 0 \\ &\dots \dots \dots \end{aligned}$$

The condition for the solution of these equations is

$$(IV) \quad \begin{vmatrix} a_{11} & a_{12} & \dots \\ a_{21} & a_{22} & \dots \\ \dots & \dots & \dots \end{vmatrix} = 0$$

that is, the determinants of the pattern of coefficients must disappear. (IV) therefore represents at the same time the boundary condition for chain explosion.

(IV) can obviously be reduced to the simple form  $\beta - \delta = 0$  only in exceptional cases. This equation is valid, as follows from what has been said before, only as long as the number of the primarily produced active centers can be disregarded as opposed to the number formed by chain-branching. If this assumption is no longer fulfilled—*e.g.*, when active centers are produced in large numbers artificially—then in at least one of the equations in (III) a member would appear accounting for the production of active centers that would be independent of  $n$ ; that is, the equation system (III) would be nonhomogeneous. In this case, equation (IV) means precisely that no solution of (III) exists; *i.e.*, under conditions under which stationarity previously still prevailed, explosion must now appear if active centers are artificially produced. We therefore do not need Semenov's hypothesis of "reciprocal chain action" in order to explain explosion by an increase in the number of initial centers.

These considerations at least show that we must be very cautious in arriving at conclusions from purely formal relations.

**5. The Time Element in the Development of a Chain Explosion.**—An explosion reaction, as we have pointed out earlier, is characterized by the fact that the reaction velocity keeps increasing with time and that nothing prevents an unlimited increase except the consumption of the

initial material. It is hardly possible in principle to draw a line of demarkation between a conversion like that shown in Fig. 161, 3, which is probably ended in a fraction of a second, and an "auto-catalytic reaction" like that shown in Fig. 161, 1, in which the reaction velocity rises over a much longer time interval, sometimes many minutes, to a correspondingly lower maximum value and then sinks correspondingly more slowly.

Semenoff differentiates between curves of type 3 and type 1 in Fig. 161 as true and degenerate explosions. Obviously the most essential characteristics of the explosion processes are common to both types.

Since the violent effects of an explosive reaction are merely secondary phenomena that are lacking, for example, in explosions at low pressures, the essential characteristic of a regular explosion is that the basic reaction takes place with a constantly increasing velocity until the consumption of the initial materials<sup>1</sup> counteracts a further velocity increase. The assumption is always that we are dealing with an exothermic reaction. If we wish to separate the regular explosion from the auto-catalytic reaction, which obviously would also come under the above definition, the following is typical of the explosion: The reaction velocity must increase by so much that the heat equilibrium is finally disturbed and, in gases, the pressure rises as a result of the rise in temperature. In Fig. 161, curve 1 would represent an auto-catalytic reaction or, according to Semenoff, a degenerate explosion. The curve shows the dependence of the reaction velocity on the duration of the reaction. Curve 2 represents explosion, since in the vicinity of point *A* the heat equilibrium is disturbed and the reaction velocity, instead of passing through the flat minimum at *B*, with increasing temperature takes a course in the direction of *B'* and then, after passing through a steeper maximum, likewise drops again. Curve 3 shows the usual type of explosion. It can as well be a matter of a heat explosion in which the heat equilibrium has been disturbed from the start and the rise in velocity is a result of the rise in temperature; but it can also be a matter of a chain explosion in which, as a result of chain-branching, the reaction velocity takes an isothermal course until it has become so great that a temperature rise results. In all

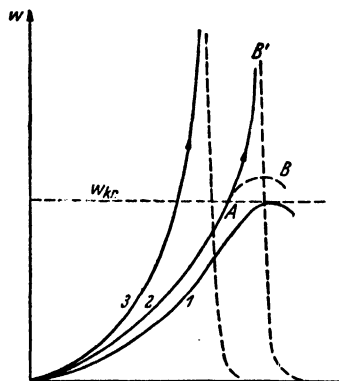


FIG. 161. --Time variations of the reaction velocity. 1. Auto-catalytic reaction. 2. Reaction with chain-branching, which changes over into thermal explosion. 3. Normal explosion.

<sup>1</sup> Or, of course, the appearance of reaction-inhibiting products.

cases, the reaction velocity passes through a maximum after a certain time and then drops to 0; for, since we are always dealing with finite quantities of substances,  $w$  cannot of course become infinitely great.

In connection with Semenov's considerations, we shall now deal with the development of an explosion in time. The induction time is especially important for practical purposes (*cf.* Chaps. XIff.). The spontaneous production of active centers in the unit of time is to amount to about  $n_0$ , the destruction by chain-breaking is  $gn$ , and the renewing by branching is  $fn$ . In all, the formation velocity of active particles therefore becomes

$$\frac{dn}{dt} = n_0 + (f - g)n \quad (64)$$

In the static case, this must be equal to zero. We shall now observe the initial period at the beginning of which (for  $t = 0$ ) let the concentration of active particles still be  $n = 0$ . Under this assumption, (64) is integrated and yields, insofar as  $n_0$ ,  $f$ , and  $g$  can be regarded as constant,

$$n = \frac{n_0}{f - g} [e^{(f-g)t} - 1] \quad (65)$$

The number of the active particles and the reaction velocity assumed (for purposes of simplicity) to be proportional to it therefore increase exponentially with the time, as might have been expected without computation. Since  $(f - g)$  can become positive (chain explosion) as well as negative (static reaction), these two cases can still be differentiated, and we can write (explosion)

$$n = \frac{n_0}{f - g} [e^{(f-g)t} - 1] \quad \text{for } f - g > 0 \quad (66)$$

and  
(static reaction)

$$n = \frac{n_0}{g - f} [1 - e^{-(g-f)t}] \quad \text{for } g - f > 0 \quad (67)$$

In the first case, the reaction velocity rises exponentially, for large  $t$ , simply as

$$Ae^{\Phi t}$$

where  $\Phi = f - g$ . This naturally holds only if  $f$  and  $g$  are regarded as constant. In reality, the branching probability will decrease as the reaction progresses, and therefore the rise in velocity will also decrease.

An S-shaped course of the conversion time curve will, by the way, result even without chain-branching if the conversion takes place by way of an intermediate product that continues to react more rapidly than it is formed (*e.g.*, aldehyde in the hydrocarbon oxidation).

Semenoff has subjected the temporal development of the reaction velocity to a still more detailed analysis<sup>1</sup> and finds (in examples taken from the literature on the subject) a remarkably good agreement with the facts, although his formulas contain fundamental simplifications. As long as more comprehensive and more recent experimental material is available to test these relations, we can omit a more detailed discussion of them here. We should like to emphasize, however, that investigating the element of time in the development of an explosion is of great importance. For many purposes, it does not suffice to know that a certain mixture explodes. It is necessary to know also in what length of time it ignites. For example, in the operation of the Otto engine, much depends on knowing that it does not knock (*cf.* Chap. XIII), *i.e.*, that the unburned portion of the compressed mixture in the combustion chamber does not react spontaneously in an extremely short time more rapidly than the flame passes through it. It is therefore important to know whether, during the time the flame requires to pass completely through the combustion chamber—for a rapidly running engine, of the order of magnitude of several thousandths of a second—the remainder of the mixture reacts or not. The problem is further complicated by the fact that neither pressure nor temperature is constant (both rise in spite of cooling by the walls as the result of continuing compression by the expanding burned gases). In addition, we are dealing not with a pure chain explosion but rather with a chain reaction with branching in which the initial acceleration is probably considerably conditioned by chain-branching, in which, of course, the heat equilibrium is disturbed (Norrish).

**6. Examples of Chain Explosions.**—Reactions in which chain-branching plays a role and the peculiar properties of these reactions have been known for some time, even though an explanation could be given only recently.

van't Hoff<sup>2</sup> gives older examples that emphatically contradict the customary assumption that the reaction velocity is proportional to the concentration of the participants in the reaction. Thereafter, in 1788, Fourcroy found that, at the usual temperature and normal pressure, pure oxygen does not affect phosphorus, whereas air oxidizes it greatly. In 1795, van Marum found that a piece of phosphorus shines much more in rarefied air than in air of ordinary pressure. H. de Labillardière observed in 1817 that hydrogen phosphide,  $\text{PH}_3$ , does not ignite on contact with air but that it explodes at ordinary temperature if the pressure is reduced. This is therefore the oldest observation of the appearance of an upper explosion limit. Analogous observations were

<sup>1</sup> Cf. "Chemical Kinetics and Chain Reactions."

<sup>2</sup> VAN'T HOFF, "Études de dynamique chimique" (Studien zur chemischen Dynamik), reworked by E. Cohen, 1896.

made by Dumas and Davy (1817). Joubert found the same for arsenic and sulphur (1874), Friedel and Ladenburg (1871) for silicon hydride, and Berthelot for nickel carbonyl; but the latter finding is questioned by Reicher and Jorissen (1894), who found ignition even at 13 atm of oxygen, insofar as we are not dealing with a third explosion limit. The oxidation velocity of  $\text{PH}_3$  in the neighborhood of the explosion limits was investigated by v. d. Stadt,<sup>1</sup> who found that, with decreasing pressure in approaching the explosion limit, the very small reaction velocity showed no increase. This reaction as well as that of phosphorus oxidation were then studied more carefully by van't Hoff himself.

The reactions of phosphorus and of  $\text{PH}_3$  with oxygen are among the first examples by which the formal relations for chain explosions could be tested, chiefly by investigations of the schools of Semenov and Hinshelwood. We shall briefly discuss these more recent findings, since they aid us in understanding the nature of the upper explosion limit.

a. *The Oxidation of Phosphorus.*—That explosive oxidation occurs only within certain pressure limits of oxygen was clear from older investigations. In this case, extreme conditions prevail since phosphorus is generally present only at its vapor pressure at room temperature of  $\sim 1/100$  mm. As Semenov<sup>2</sup> and his collaborators have shown, it is possible to detect the lower pressure limit strikingly if oxygen is permitted to flow through a capillary tube into an evacuated reaction vessel containing solid phosphorus. In a given reaction vessel, the critical lower explosion limit occurred at an oxygen pressure of  $1/20$  mm Hg. If oxygen was allowed to flow into the evacuated vessel containing phosphorus, the pressure first rose to this point without reaction on the part of the oxygen. When the critical pressure is reached, reaction sets in with illumination, and the pressure does not rise even if more oxygen flows in, because all the oxygen present beyond the critical limit is precipitated with phosphorus as a nonvolatile oxide. Oxygen, slightly under the critical pressure, did not react noticeably with phosphorus for several hours. The same critical explosion pressure was determined when oxygen was passed over phosphorus below the critical pressure and then suddenly compressed. If, instead of additional oxygen, argon is added to the phosphorus and oxygen at a lower pressure than the lower explosion limit,<sup>3</sup> it is possible to obtain explosion just as it would be with  $\text{O}_2$ . This remarkable result is to be expected according to the chain theory, if the chains are broken at the wall; for then argon too must retard the diffusion to the wall and therefore also retard the chain-breaking. The critical explosion pressure was found to be proportional to the square of the

<sup>1</sup> V. D. STADT, J., *Z. physik. Chem.*, **12**, 322 (1893).

<sup>2</sup> SEMENOV, N., *Z. Physik*, **46**, 109 (1927).

<sup>3</sup> CHARITON and WALTA, *Z. Physik*, **39**, 547 (1926).

chamber diameter, as could likewise be predicted for chain-breaking at the wall (insofar as the breaking probability is not extremely small) cf. Table 44.

TABLE 44.—LOWER EXPLOSION LIMIT IN PHOSPHORUS OXIDATION (FROM SEMENOFF)

| Diameter of the spherical reaction chamber $d$ , cm | $p_{cr}(\text{O}_2)$ , mm Hg | $p_{cr}d^2$ |
|---|------------------------------|-------------|
| 6   | $3.27 \cdot 10^{-3}$         | 190         |
| 13.4  | $1.16 \cdot 10^{-3}$         | 209         |
| 18.1  | $0.61 \cdot 10^{-3}$         | 200         |

As an empirical relation that yields the explosion limit with varying pressures of phosphorus, oxygen, and added argon as well as in dependence on the diameter of the chamber, the following was found:

$$d^2 p_{\text{P}_4} p_{\text{O}_2} \frac{p_{\text{P}_4} + p_{\text{O}_2} + p_{\text{A}}}{p_{\text{P}_4} + p_{\text{O}_2}} = C_1 \quad (68)$$

In this,  $C_1$  had a value of  $1.25 \cdot 10^{-3}$  for a cylindrical reaction vessel, if  $d$  is given in centimeters and the pressure of the various gases in mm Hg.

An expression of the above form for the lower explosion limit, which is also valid for other cases, can be derived in the following manner, according to Semenoff. We have already derived the fact that, in chain-breaking at the wall, the breaking velocity is proportional to the diffusion coefficient (which is inversely proportional to the total pressure that appears in the numerator of the above formal expression) and inversely proportional to the square of the diameter of the container  $d$ . We shall verify this result in detail with Semenoff, using Smoluchowski's relations as a point of departure.<sup>1</sup> According to Smoluchowski, the number of collisions that a particle of gas experiences in a displacement of a distance of  $\Delta x$  is

$$\nu = \frac{3\pi \Delta x^2}{4\lambda^2} \quad (69)$$

if  $\lambda$  is the free length of path.

This formula can be obtained in the following way (up to a numerical factor of the order of magnitude 1, which does not concern us here). For displacement to the extent of the distance  $\Delta x$ , let the particle require the time  $t$ . During this time, the particle has moved along its zigzag path in all  $tw$  cm, if  $w$  is its velocity. Since it experiences a collision every  $\lambda$  cm as an average, it has experienced during this time

$$\nu = \frac{tw}{\lambda}$$

<sup>1</sup> V. SMOLUCHOWSKI, M., *Ann. Physik.*, (4), 21, 756 (1906).

collisions. In order to make use of this result, we must know how long the time  $t$  is which it needs for displacement of  $\Delta x$ . If we introduce as an approximation the average square of displacement  $\overline{\Delta x^2}$  (which is not identical with the square of the average displacement), we can use the relation valid for this

$$\overline{\Delta x^2} = 2Dt \quad t = \frac{\overline{\Delta x^2}}{2D}$$

If in place of the diffusion coefficient  $D$  we use the approximate expression

$$D \cong \frac{\lambda w}{3}$$

we finally obtain

$$\nu \cong \frac{3}{2} \frac{\Delta x^2}{\lambda^2} \quad (70)$$

which, except for one factor  $\pi/2$ , is identical with the above expression.

The average number of impacts that any particle in a container of the thickness  $d$  experiences in diffusion up to the wall will therefore be proportional to  $d^2/\lambda^2$ , in which the added numerical factor is somewhat smaller than the above (and depends on the form of the container), since on the average a molecule was less than  $d/2$  distance from the wall. We can omit computing this factor ( $\pi/16$  for a container with planiparallel walls with a distance  $d$  between them), since we shall not make use of it.

If an active particle were to be formed at a distance  $d$  from the wall and react in a chain reaction taking place at every impact, the length of the chain  $\nu$  would be equal to the number of impacts before hitting the wall, in other words (approximately),

$$\nu \cong \frac{3\pi}{4} \frac{d^2}{\lambda^2}$$

In reality, an active particle will react not at every impact but rather on the average at every  $q$ th impact; then the chain length is only

$$\nu' \cong \frac{3\pi}{4} \frac{d^2}{\lambda^2 q}$$

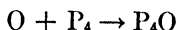
The free length of path  $\lambda$  is inversely proportional to the pressure, or, more precisely, if various types of molecule  $M_1, M_2, \dots$  with the partial pressures  $p_1, p_2, \dots$  are present, if  $\lambda$  is the free length of path and  $\lambda_{01}$  the free length of path of the active particles in pure  $M_1$  with standard pressure, etc.,

$$\frac{1}{\lambda} \cong \frac{p_1}{\lambda_{01}} + \frac{p_2}{\lambda_{02}} + \dots$$

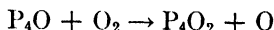
(The effective cross sections in a gas mixture that bound the free length of path and are inversely proportional to it must be added.) We should then obtain for the length of the chain

$$\nu' \sim \frac{d^2}{q} \left( \frac{p_1}{\lambda_{01}} + \frac{p_2}{\lambda_{02}} + \dots \right)^2$$

If the types of molecule  $M_1$  and  $M_2$  are the reacting materials and if an active particle experiences  $q$  collisions in a mixture of both until it reacts, then it will experience more collisions, namely,  $q'$ , till it reacts, if an inactive component  $M_3$  is added, since all collisions with  $M_3$  are ineffective. If especially two types of active particles are present, *e.g.*, O and  $P_4O$ , of which one type reacts<sup>1</sup> with  $P_4$ ,



and the other type with  $O_2$ ,



then the number of impacts in the mixture after which on the average a reaction takes place will be  $q_1$  and  $q_2$ .

If  $q_1^0$  is the number of impacts that O requires for reaction in pure phosphorus vapor, and correspondingly  $q_2^0$  is the number that  $P_4O$  requires in pure oxygen, then

$$q_1 = q_1^0 \frac{\frac{p_1}{\lambda_{01}} + \frac{p_2}{\lambda_{02}} + \frac{p_3}{\lambda_{03}}}{\frac{p_1}{\lambda_{01}}}$$

$$q_2 = q_2^0 \frac{\frac{p_1}{\lambda_{01}} + \frac{p_2}{\lambda_{02}} + \frac{p_3}{\lambda_{03}}}{\frac{p_2}{\lambda_{02}}}$$

In this, we have equated the corresponding lengths of path for O and  $P_4O$ . For more precise computation (which would, however, be required only in rarest cases), they would be different. For simplicity, we shall also assume the  $\lambda$  values as equal for all reaction partners and inert gases. They then drop out entirely from equations for  $q$ . If we now have a reaction chain in which O and  $P_4O$  appear alternately as chain agents, then the effective  $q$  of the average value of the above entities becomes

$$q = \frac{q_1 + q_2}{2} = \left( \frac{q_1^0}{p_1} + \frac{q_2^0}{p_2} \right) \frac{p_1 + p_2 + p_3}{2}$$

Since

$$\frac{1}{\lambda} = \frac{p_1}{\lambda_{01}} + \frac{p_2}{\lambda_{02}} + \frac{p_3}{\lambda_{03}}$$

the chain length becomes (let  $\lambda_{01} \cong \lambda_{02} \cong \lambda_{03}$ )

$$v' \sim \frac{d^2}{\lambda^2 q} = \frac{d^2}{\lambda_0^2} (p_1 + p_2 + p_3) \frac{2}{\frac{q_1^0}{p_1} + \frac{q_2^0}{p_2}}$$

<sup>1</sup> We are here concerned only with a mechanism with which we can verify the relations forcibly. We shall refrain from any definite statement as to the actual mechanism. In the meantime, the cold phosphorus flame has been investigated more thoroughly spectroscopically [RUMPF, K., *Z. physik. Chem.*, Sec. B, **38**, 469 (1933)], and the band spectrum in the visible (chiefly in the green) has been ascribed to an agent PO, which is thought to originate in a collision between  $P_2$  and  $O_2$ .



If we substitute for further simplification  $q_1^0 = q_2^0 = q_0$ , then

$$\nu' \sim \frac{d^2}{\lambda_0^2 q_0^2} \frac{p_1 + p_2 + p_3}{p_1 + p_2} p_1 p_2 = \frac{d^2 p_1 p_2}{\lambda_0^2 q_0^2} \left( 1 + \frac{p_3}{p_1 + p_2} \right) \quad (71)$$

Now let  $\delta$  be the probability that the chain will branch at some link, then

$$\nu' \delta = 1 \quad (72)$$

clearly explosion, for then a new chain is started on the average for each chain that has run its course. The chain will never stop. If we assume (completely justified by the result) that  $\delta$  is independent of the concentration of the individual reaction partners, then the condition for explosion following from (71) and (72) is

$$\frac{d^2 p_1 p_2}{\lambda_0^2 q_0^2} \left( 1 + \frac{p_3}{p_1 + p_2} \right) = C_1 \quad (73)$$

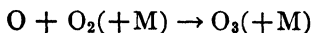
in which  $C_1$  can be dependent only on the temperature. If we identify  $p_1, p_2, p_3$  with  $p_{P_4}, p_{O_2}, p_A$ , then this is exactly the empirically discovered explosion condition. Consideration of the individual impact cross sections would lead to furnishing the individual  $p$ 's in brackets with individual factors, as was found experimentally by Melville and Ludlam.<sup>1</sup>

For the upper pressure limit of the oxidation of phosphorus, the following is found:

$$\frac{p_{P_4}}{p_{O_2}} = C_2$$

in which at room temperature  $C_2 = 2.8 \cdot 10^{-5}$ ; *i.e.*, with a vapor pressure of phosphorus of  $\sim \frac{1}{100}$  mm, the upper critical pressure limit for oxygen is  $\sim 280$  mm. The upper limit is, as is generally observed, independent of the diameter of the chamber. Kowalsky<sup>2</sup> determined this experimentally by filling a reaction chamber with oxygen until it was above the critical explosion pressure as long as the phosphorus in it was frozen out with liquid air. Then only was the desired vapor pressure of the phosphorus freed. The oxygen was thereupon slowly pumped off, and the pressure at which explosion occurred was determined.

For an explanation of the upper limit, a destruction of active centers in the gas phase must be assumed. How the breaking comes about is not clear in detail, especially since the nature of the chain agents has not yet been determined in this reaction. Kowalsky assumed that impurities in the oxygen are responsible for the breaking, for which view it is possible to adduce experiments with artificially added impurities (see below). For breaking in the gas phase with pure oxygen, the triple collision reaction



<sup>1</sup> MELVILLE, H.W., and E.B. LUDLAM, *Proc. Roy. Soc. London*, **132**, 108 (1931).

<sup>2</sup> KOWALSKY, *Z. physik. Chem., Sec. B*, **4**, 288 (1929).

might be considered. Even though the appearance of O-atoms as active particles at room temperature may not seem plausible, the well-known observation might be adduced in its favor that, in the slow oxidation of phosphorus, ozone is found as a reaction product. We shall dispense with quantitative considerations here, but it is possible to derive formal relations for breaking by means of impurities as well as by means of triple collisions with  $O_2$  which coincide with experimental findings. By considering all the possibilities of breaking, it is possible to formulate a single relation that represents the entire range of explosion, upper and lower limit as well as the transitional range, as has been discussed in detail by Semenoff ("Chemical Kinetics and Chain Reactions").

Experiments with additions of various foreign gases can be regarded as support for these views. In his experiments, Kowalsky found that the upper limit could be reproduced only if he worked with constantly new reaction chambers; repetition of an experiment in the same chamber at the upper pressure limit yielded an extension of the reaction range. Since the position of the upper limit is in itself independent of the dimensions of the chamber and should also be independent of the nature of the wall, this influence might be due to impurities that are introduced by the preceding reaction, under certain circumstances by ozone. At any rate, the intentional addition of ozone extends the explosion range, as Kowalsky has shown. The effect of other additions has been investigated by Tauss and Görlacher.<sup>1</sup> According to Semenoff, two influences play a part: In additions of inert gases (argon or nitrogen), there is a lowering of the upper pressure limit of oxygen only by means of the triple collision effect of the added gas. On the other hand, additions that are effective as "poisons" in small quantities, like ethylene and other olefins, iron carbonyl, etc., apparently react directly by the consumption of chain agents. These results all fit into Semenoff's equations (cf. also Melville).<sup>2</sup>

The slow reaction below the lower explosion limit likewise seems to submit to the above laws. Melville and Ludlam<sup>3</sup> studied the (very slow) reaction below the lower pressure limit by introducing a heated platinum or tungsten wire into the gas. The reaction, which takes place with the platinum wire at 200°, is obviously only a surface reaction and hence of little interest. With tungsten, it takes place at 500° with a velocity convenient to observe. We find the same equation for the velocity as is valid for the lower explosion limit—proportionality with the square of the chamber diameter, corresponding dependence on the partial pressures of the individual gases, etc. The reaction is also connected with chemiluminescence of the gas, and it may therefore be assumed that the

<sup>1</sup> TAUSS and GÖRLACHER, *Z. anorg. Chem.*, **190**, 95 (1930).

<sup>2</sup> MELVILLE, H.W., *Trans. Faraday Soc.*, **28**, 1 (1932).

<sup>3</sup> MELVILLE, H.W., and E.B. LUDLAM, *Proc. Roy. Soc. London, A*, **135**, 315 (1932).

reaction chains are induced on the tungsten filament, proceed in the gas phase, and break at the wall. The velocity expression is

$$-\frac{dp_{O_2}}{dt} = kp_{P_4}p_{O_2} \left( 1 + \frac{\mu p_x}{p_{P_4} + p_{O_2}} \right) d^2 e^{-E/RT}$$

where  $p_x$  is the pressure of the inert gas. The activation energy  $E$  was found to be 16 kcal. To which elementary process it belongs is not clear.

*b. The Combustion of Hydrogen Phosphide.*—The combustion of  $PH_3$  takes a course similar to that of phosphorus and likewise shows two explosion limits. The lower limit, however, other conditions being equal, is about 1000 times higher than for phosphorus. For the explosion limits, the equations are similar to those of phosphorus, and they can be formally derived in the same way, even though here too the exact nature of the chain agents and the elementary reactions is not precisely known. For details, the individual works should be consulted.<sup>1</sup> Of the other explosions that show typical explosion limits as a result of chain-branching, we shall mention only the combustion of sulphur,<sup>2</sup> the combustion of carbon disulphide,<sup>3</sup> and the combustion of hydrogen sulphide,<sup>4</sup> and the chlorine detonating gas explosion in light.<sup>5</sup>

<sup>1</sup> DALTON, R.H., and C.N. HINSHELWOOD, *Proc. Roy. Soc. London, A*, **125**, 294 (1929). DALTON, R.H., *Proc. Roy. Soc. London, A*, **128**, 263 (1930). HINSHELWOOD, C.N., and K. CLUSIUS, *Proc. Roy. Soc. London*, **129**, 589 (1930). MELVILLE, H.W., and H.L. ROXBURGH, *J. Chem. Phys.*, **2**, 739 (1934); *Nature*, **131**, 690 (1933). TRAUTZ, M., and GABLER, *Z. anorg. Chem.*, **180**, 321 (1929). MELVILLE, H.W., *Trans. Faraday Soc.*, **28**, 308 (1932); *Proc. Roy. Soc. London, A*, **138**, 374 (1932); **139**, 541 (1933). Cf. also the discussion in N. Semenov, "Chemical Kinetics and Chain Reactions," and L.S. Kassel, "Kinetics."

<sup>2</sup> NORRISH and RIDEAL, *J. Chem. Soc.*, **123**, 3203 (1923). NEUMANN, K., *Ber. deut. chem. Ges.*, **16**, 139 (1888). WATSON, *Chem. News*, **108**, 787 (1913). EMELEUS, H.M., *J. Chem. Soc.*, 1928, p. 1942. SEMENOFF, N., and RJABININ, *Z. physik. Chem.*, Sec. B, **1**, 122 (1928). RITCHIE, A., and E.B. LUDLAM, *Proc. Roy. Soc. London, A*, **138**, 635 (1932).

<sup>3</sup> THOMPSON, H.W., *Z. physik. Chem.*, Sec. B, **10**, 273 (1930). *J. physik. Chem.*, **35**, 3639 (1931). THOMPSON, H.W., and C.F. KEARTON, *Z. physik. Chem.*, Sec. B, **14**, 359 (1931). TAYLOR, H.A., and E.M. LIVINGSTON, *J. physik. Chem.*, **35**, 2676 (1931). THOMPSON, H.W., and KELLARD, *J. Chem. Soc.*, 1931, p. 1809. RITCHIE, A., R.H. BROWN, and J.J. MUIR, *Proc. Roy. Soc. London, A*, **137**, 511 (1932). FOWLER, A., and W.M. VAIDYA, *Proc. Roy. Soc. London, A*, **132**, 310 (1931). GILL, F., E.W. MARDLES, and H.C. TETT, *Trans. Faraday Soc.*, **24**, 574 (1928). KONDRATJEV, V., *Z. Physik*, **63**, 322 (1930). PRETTRE, M., and P. LAFFITTE, *Compt. rend.*, **190**, 796 (1930). For older works on  $CS_2$  combustion, see Bone and Townend, "Flame and Combustion," pp. 414ff.

<sup>4</sup> FARKAS, L., *Z. Elektrochem.*, **37**, 670 (1931). HARTECK, P., and U. KOPSCH, *Z. physik. Chem.*, Sec. B, **12**, 327 (1931). LAFFITTE, P., and BARET, *Bull. soc. chim.*, (4), **5**, 281 (1932). LEICESTER, F.D., *J. Soc. Chem. Ind.*, **52**, *Chem. Ind.*, **11**, 341 (1933).

<sup>5</sup> KOKOTSCHASCHWILI, V., *Z. physik. Chem.*, Sec. B, **23**, 431 (1933). Cf. also SEMENOFF, N., *Z. physik. Chem.*, Sec. B, **28**, 43 (1935).

It might be mentioned that, in accounting for the upper explosion limits, another explanation was considered before it was generally assumed that a deactivation in the gas phase was the cause. That explanation concerned the action of the absorption layer, since, as can be shown directly in certain cases, the chains can also be induced at the wall (Haber, Alyea<sup>1</sup>). However, that explanation was generally abandoned after an explanation for the phenomena could be given by gas-phase deactivation in those cases for which quantitative measurements existed. Occasionally, nevertheless, such phenomena will also have to be borne in mind.

<sup>1</sup>ALYEA, H., and F. HABER, *Z. physik. Chem., Sec. B*, **16**, 193 (1930). *Naturwissenschaften*, **18**, 44 (1930). ALYEA, H., *J. Am. Chem. Soc.*, **53**, 1324 (1931).

## CHAPTER IX

### COMBUSTION OF OXYGEN-HYDROGEN MIXTURES AND CARBON MONOXIDE

#### A. COMBUSTION OF OXYGEN-HYDROGEN MIXTURES<sup>1</sup>

The combustion of oxygen-hydrogen mixtures has naturally interested the chemist for a long time, and it is not surprising that the first investigations in this field occurred more than 100 years ago. These experiments, however, were concerned chiefly with the catalytic reaction, which is interesting to be sure, but its treatment lies outside the range of this book. For these older investigations, we refer to Bone,<sup>2</sup> Hinshelwood and Williamson,<sup>3</sup> or Mittasch.<sup>4</sup>

The first of modern investigations of the combustion of oxygen-hydrogen mixtures is that of Bodenstein.<sup>5</sup> He investigated the conversion of flowing oxygen-hydrogen in porcelain tubes of various forms and various ratios of surface to volume. The reaction can be observed even at  $\sim 600^\circ$  without explosion. As a velocity equation under the special conditions, we obtain the simple time law of the third order

$$\frac{d[\text{H}_2\text{O}]}{dt} = k[\text{H}_2]^2[\text{O}_2]$$

which, however, is not always valid. Since it developed that, with various forms of containers, the reaction velocity essentially changed with the surface of the container, it followed that also in this case the wall reaction generally predominated. For more recent investigations on catalytic oxidation, we refer to the books by Bone and Hinshelwood.

Investigations mentioned in Chap. I (by Falk, Cassel, and Dixon) revealed that explosion in oxygen-hydrogen appears at  $\sim 500^\circ$  to  $600^\circ\text{C}$ . Systematic investigations by Dixon and his collaborators also established the dependence of the ignition temperature on pressure as well as on the length of the induction periods that occur before ignition with known

<sup>1</sup> Cf. in this connection KASSEL, L.S., *Chem. Rev.*, **21**, 331 (1937). LEWIS and v. ELBE, "Combustion, Flames and Explosions of Gases."

<sup>2</sup> BONE and TOWNEND, "Flame and Combustion in Gases."

<sup>3</sup> HINSHELWOOD, C.N., and A.T. WILLIAMSON, "The Reaction between Hydrogen and Oxygen," Oxford, 1934.

<sup>4</sup> MITTASCH, A., and THEIS, E., "Von Davy u. Döbereiner bis Deacon: Ein halbes Jahrhundert Grenzflächenkatalyse," Verlag Chemie, Berlin, 1932.

<sup>5</sup> BODENSTEIN, M., *Z. physik. Chem.*, **29**, 665 (1899).

composition and temperature. The observations extend to induction periods between 0.5 and 15 sec. The lengthening of the induction period from the former to the latter value results in a lowering of the ignition temperature by  $\sim 50^{\circ}\text{C}$ . From experiments by Dixon, it may be concluded that we are dealing with chain-branching at least in a part of the range investigated; for the ignition temperature rises from 75 mm to about 1 atm of pressure, and it drops again only at still higher pressures, at first very slowly, which suggests that the transition to thermal explosion is gradually taking place. In the last decade, oxygen-hydrogen combustion has been the object of numerous studies. The explosion range has the typical form of chain explosion (Fig. 162). Since the position of the lower limit is very dependent on the dimensions of the chamber and the condition of the wall, the values given in Fig. 162 can offer only a point of departure for normal conditions. We shall discuss details later. The slow reaction has been investigated both below the lower and above the upper explosion limit. In both cases, rather complicated laws prevail (also the above-mentioned older works by Bodenstein belong to the range above the upper explosion limit).

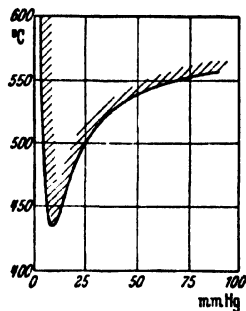


FIG. 162.—Critical explosion limits for oxygen-hydrogen mixture,  $2\text{H}_2 + \text{O}_2$ .

Greater strides have been made in the explanation of oxygen-hydrogen than in the explanation of the chain explosions discussed earlier, although by no means all the questions can be regarded as having been answered. That greater strides have been made is to be attributed not only to the great amount of work that was done precisely on this reaction, but more especially to the fact that the investigators were not content with gaining formal relations for explosions limits and reaction velocities outside these limits but obtained a direct insight into the elementary processes involved in conversion by the aid of spectroscopic and photochemical measurements as well as by experiments with free atoms and radicals. For somewhat more complicated reactions—for hydrocarbon combustion, to be treated later, even more than for oxygen-hydrogen combustion—it is generally true that the formal laws observed in kinetics do not suffice alone to select with certainty those of a large number of possible elementary processes which account for the real reaction mechanism. For an understanding of the total process, we shall therefore be compelled to discuss a portion of these spectroscopic, photochemical, etc., investigations.

**1. The Lower Explosion Limit.**—The lower limit of oxygen-hydrogen has often been investigated. The results of the various authors vary

considerably, a fact that is to be expected, since the position of the lower limit is largely determined by the nature of the wall. The experimental procedure is generally as follows: Premixed gases are introduced into the heated reaction container, and the minimum pressure at which they just ignite is observed. The appearance of ignition is not always easy to determine at the lower limit, either by the illumination of the gas or, and this is more certain, by the rise in pressure with a sufficiently sensitive manometer. Semenov occasionally introduced the gases into the container at a point above the critical pressure limit and determined the remaining pressure of the reaction partner after the appearance of explosion. This method at first appears somewhat questionable, but no systematic variations from other experiments were noted. It is also possible to determine the explosion limit with gases flowing at low pressure.

Hinshelwood and Moelwyn-Hughes<sup>1</sup> found explosion limits for various container diameters  $d$  for mixtures consisting of  $2\text{H}_2 + \text{O}_2$  at  $500^\circ\text{C}$  (see Table 45). The product  $pd$  is reasonably constant but with varia-

TABLE 45 — EXPLOSION LIMITS FOR MIXTURES OF  $2\text{H}_2 + \text{O}_2$  AT  $500^\circ\text{C}$  AND WITH VARIOUS CHAMBER DIAMETERS  $d$

| $d$ , mm | $p$ , mm Hg | $pd$ |
|----------|-------------|------|
| 54       | 1.06        | 57   |
| 49       | 0.91        | 45   |
| 32       | 2.85        | 91   |
| 18       | 3.64        | 65   |

tions up to 50 per cent of the average. Insofar as the reaction is especially sensitive to the condition of the wall, such great variations are not surprising. In chain-breaking at the wall and constant composition of the mixture, constancy of the product  $pd$  at the limit is to be expected; for, if two types of chain agent are present of which one reacts with  $\text{H}_2$  and the other with  $\text{O}_2$ , we can formally repeat the same computations that we made for phosphorus combustion (page 285) and thus reach the condition for explosion

$$[\text{O}_2][\text{H}_2]d^2 \left\{ 1 + \frac{[\text{X}]}{[\text{O}_2] + [\text{H}_2]} \right\} = \text{const}$$

As long as no inert gas  $[\text{X}]$  is added and the mixture ratio  $[\text{H}_2]:[\text{O}_2]$  is kept constant, this leads to

$$p^2d^2 = \text{const}$$

or

$$pd = \text{const} \quad (1)$$

<sup>1</sup> HINSHELWOOD, C.N., and MOELWYN-HUGHES, *Proc. Roy. Soc. London, A*, **138**, 311 (1932).

If we kept the pressure of a component at a constant low value (as is the case in phosphorus combustion) and changed only the pressure of the others, we should have instead of (1)

$$pd^2 = \text{const} \quad (2)$$

According to the conditions of experiment, therefore, it is possible to obtain both relations for the explosion limits.

The position of the lower limit depends a great deal on the nature of the wall. Thus the lower explosion limit at 500° in quartz and pyrex containers cleaned with distilled water showed pressures of a few mm Hg. Frost and Alyea<sup>1</sup> found essentially higher limit pressures at the same temperature in pyrex containers that were washed out with a 10 per cent KCl solution; 15 to 20 mm Hg; and Semenowa reports<sup>2</sup> that Kowalsky succeeded in obtaining, in vessels that had been subjected to an electrical discharge, pressure limits of only  $\sim \frac{1}{10}$  of those usually obtained, namely, of only a few tenths of a millimeter. The condition of the wall can thus result in a change of the lower pressure limit by almost 100.

TABLE 46.—CRITICAL EXPLOSION LIMITS OF MIXTURES OF  $\text{H}_2 + \text{O}_2$  IN ENAMELED PYREX TUBES OF VARIOUS DIAMETERS (FROM N. SEMENOWA)

| $d$ , mm | $t = 585^\circ\text{C}$ |      | $t = 482^\circ\text{C}$ |     | 440°C |      |
|----------|-------------------------|------|-------------------------|-----|-------|------|
|          | $p^*$                   | $pd$ | $pd$                    | $p$ | $p$   | $pd$ |
| 5.8      | 16                      | 93   | 28                      | 160 | 42    | 244  |
| 10.2     | 10                      | 102  | 18                      | 190 | 28    | 285  |
| 15.7     | 8                       | 125  | 14                      | 220 | 20    | 314  |
| 20.0     | 6                       | 120  | 10                      | 200 | 15    | 300  |
| 30.0     | 4                       | 120  | 7                       | 210 | 10    | 300  |

\* Pressure figures in scale divisions; 14 scale divisions = 0.46 mm Hg.

If several successive experiments are conducted in the same new container, the pressure limit is lowered from experiment to experiment. All this was systematically studied by N. Semenowa.<sup>1</sup> She used tubes consisting of especially enameled pyrex glass that yielded an extremely low and temporarily constant breaking probability, similar to the tubes that were subjected to an electrical discharge. With these, she obtained quite low explosion limits that could easily be reproduced. For observation, she used an especially sensitive glass-membrane manometer. Numerical values from experiments with five containers of various diameters are given in Table 46; the product  $pd$  is quite constant. For these conditions of extremely small breaking probability, the relation

<sup>1</sup> FROST, A.A., and N.H. ALYEA, *J. Am. Chem. Soc.*, **55**, 3227 (1933).

<sup>2</sup> SEMENOWA, N., *Acta Physicochim. URSS*, **6**, 25 (1937).



requires a special discussion. The case of Kassel and Storch<sup>1</sup> must be operative, in which diffusion no longer plays a role but the total number of chain-breakings is given by the number of impacts against the wall times the breaking probability per shock,  $\epsilon$ , and the number of the branchings is proportional to the volume. The diameter of the container is preserved in the resulting relation because the ratio volume : surface is proportional to it. A relation of that kind is obtained only with very small values of  $\epsilon$  (about  $10^{-4}$  or smaller, since it depends on the ratio of free length of path to the diameter of the container). For  $\epsilon \sim 10^{-1}$  to  $10^{-2}$ , the conditions approaching  $\epsilon = 1$  are not much changed under normal conditions (see Kassel and Storch as well as Lewis and v. Elbe, cited page 273). The reason might be that a particle that diffuses to

TABLE 47.—EXPLOSION LIMITS OF  $3\text{H}_2 + 2\text{O}_2$  MIXTURES IN ENAMELED PYREX TUBES AND IN QUARTZ TUBES IN DEPENDENCE ON ARGON ADDITIONS (FROM BIRON AND NALBANDJAN)

| $t = 515^\circ\text{C}$ |                                     | $t = 485^\circ\text{C}$ |                                     |
|-------------------------|-------------------------------------|-------------------------|-------------------------------------|
| $p_{\text{Argon}}$      | $p_{\text{H}_2+\text{O}_2}$ , mm Hg | $p_{\text{Argon}}$      | $p_{\text{H}_2+\text{O}_2}$ , mm Hg |
| —                       | 0.15                                | —                       | 0.23                                |
| 0.04                    | 0.15                                | 0.057                   | 0.228                               |
| 0.07                    | 0.14                                | 0.12                    | 0.24                                |
| 0.105                   | 0.145                               | 0.18                    | 0.23                                |
| 0.15                    | 0.15                                | 0.235                   | 0.235                               |

TABLE 48.—EXPLOSION LIMITS OF TABLE 47 IN A QUARTZ CHAMBER AT  $515^\circ\text{C}$

| Without rinsing with $\text{O}_2$ |                                     | After rinsing with $\text{O}_2$ |                                     |
|-----------------------------------|-------------------------------------|---------------------------------|-------------------------------------|
| $p_{\text{Argon}}$                | $p_{\text{H}_2+\text{O}_2}$ , mm Hg | $p_{\text{Argon}}$              | $p_{\text{H}_2+\text{O}_2}$ , mm Hg |
| —                                 | 11.2                                | —                               | 11.2                                |
| 8.5                               | 8.5                                 | 8.23                            | 8.23                                |
| 14.5                              | 7.3                                 | 13.9                            | 6.9                                 |
| 20.5                              | 6.9                                 | 19.2                            | 6.4                                 |

the wall and has collided against it in general experiences a greater number of collisions with the wall until it again diffuses into the center. The breaking probability  $\epsilon$  therefore becomes decisive only when it is very small as compared with unity.

Since diffusion no longer plays a role in case of extremely small breaking probabilities (the concentration of active particles practically

<sup>1</sup> KASSEL, L.S., and H.H. STORCH, *J. Am. Chem. Soc.*, **57**, 672 (1935) (cf. LEWIS and v. ELBE, cited p. 273).

becomes constant in the entire volume), even the addition of foreign gas might no longer be of influence on the explosion limits under these conditions. This has been tested by Biron and Nalbandjan under conditions analogous to those in Semenowa's experiments.<sup>1</sup> In enameled pyrex tubes, the critical explosion pressure is actually independent of the addition of argon; whereas, in quartz tubes with high breaking probability, the usually observed dependence on the presence of inert gases is present. This is apparent from the experiments in Tables 47 and 48. As has already been mentioned on page 273, the conditions in which  $\epsilon < 1$  can be treated quantitatively, as Kassel and Storch (cited page 273) and Lewis and v. Elbe<sup>2</sup> have shown. The difficulty in the application of the quantitative relations consists in the fact that  $\epsilon$  is in general unknown and that we must further take into account the possibility of a change of  $\epsilon$  from experiment to experiment. We shall therefore be able to content ourselves in most cases with semiquantitative relations and the use of formulas valid for the borderline cases with  $\epsilon$  not too small and very small.

If no entities dependent on the temperature, except the branching probability, are contained in the expression for the lower limit, their activation heat would determine the position of the lower explosion limit (and also analogously, the upper) at various temperatures;<sup>3</sup> for, if we write the explosion condition in the form (cf. page 288)

$$\nu\delta = 1$$

where  $\nu$  is the average chain length and  $\delta$  the probability of branching per chain link, and if we assume from earlier relations that  $\nu$  is proportional to  $p^2$  and  $\delta$  proportional to  $e^{-E/RT}$ , we obtain as the condition of explosion

$$p^2 e^{-E/RT} = \text{const}$$

$$p \sim e^{+E/2RT}$$

whereas with similar assumptions (cf. pages 276, 277, 300, 328) we should obtain for the upper explosion limit

$$p \sim e^{-E/RT}$$

Under these special assumptions, the temperature dependencies of the lower and upper explosion limits are coupled with one another, and the lower limit changes only half as much with the temperature as the upper, and in the opposite direction.

<sup>1</sup> BIRON, A., and A. NALBANDJAN, *Acta Physicochim. URSS*, **6**, 43 (1937).

<sup>2</sup> LEWIS, B., and G. V. ELBE, *J. Am. Chem. Soc.*, **59**, 970 (1937); also "Combustion, Flame and Explosion of Gases."

<sup>3</sup> Cf in this connection SEMENOFF, "Chemical Kinetics and Chain Reactions." SEMENOWA, quoted p. 295.

TABLE 49.—LOWER EXPLOSION LIMIT FOR OXYGEN-HYDROGEN MIXTURES (FROM HINSHELWOOD AND MOELWYN-HUGHES)

|                  |      |      |      |      |
|------------------|------|------|------|------|
| $t$ , °C.....    | 650  | 604  | 550  | 500  |
| $p$ , mm Hg..... | 2.99 | 2.74 | 2.75 | 3.62 |

The experiments confirm this conclusion insofar as the lower limit is actually much less dependent on the temperature than the upper (cf. Fig. 162). However, in a quantitative respect there are great discrepancies between the findings of different authors.

Hinshelwood (quoted pages 292, 294) finds the lower limit above 550° practically independent of the temperature (Table 49).

On the other hand, Semenov, Sagulin, Kowalsky, and Kopp<sup>1</sup> found a greater dependence on the temperature, although, to be sure, in the lower temperature range where the transition to the upper limit takes place, namely,  $\sim 9$  mm at 440°, 4.5 mm at 500°, and 3 mm at 550°. These values agree fairly well with comparable data obtained by Hinshelwood. It is uncertain how much physical importance should be attributed to the activation heat derived from this,  $E' = 14$  kcal. It would fit very well with that found for the upper limit,  $E \sim 22$  to 26 kcal, if  $E' = \frac{1}{2}E$  (cf. pages 297 and 300).

TABLE 50

| $p_{H_2}$ , mm | $p_{O_2}$ , mm | $p_{H_2O_2}$ |
|----------------|----------------|--------------|
| 3.12           | 0.78           | 2.43         |
| 2.30           | 1.15           | 2.64         |
| 1.65           | 1.65           | 2.72         |
| 1.07           | 2.14           | 2.29         |
| 0.86           | 3.44           | 2.96         |

TABLE 51.—LOWER EXPLOSION LIMIT FOR  $H_2 + O_2$  IN DEPENDENCE ON HELIUM AND ARGON ADDITIONS (FROM HINSHELWOOD AND MOELWYN-HUGHES)

| Helium   |          | Argon |      |
|----------|----------|-------|------|
| $p_{He}$ | mm $H_2$ | $p_A$ | $p$  |
| 0        | 3.33     | 0     | 4.25 |
| 5.45     | 2.73     | 2.90  | 2.90 |
| 8.70     | 2.18     | 4.41  | 2.21 |
| 0        | 3.52     | 6.72  | 1.68 |
|          |          | 6.51  | 1.09 |
|          |          | 0     | 4.20 |

<sup>1</sup> SEMENOV, SAGULIN, KOWALSKY, and KOPP, *Z. physik. Chem.*, Sec. B, **6**, 307 (1930).

Semenowa, from her experiments, derives the activation heat for the lower limit as  $E \sim 11$  kcal, which is in agreement with the foregoing. The discrepancies, especially from Hinshelwood's experiments, are not to be taken seriously, considering the neglected factors as well as the fact that no account was taken of temperature dependence of the breaking yield at the wall (which is hardly capable of being verified).

At constant temperature and given diameter of the container, the following should be valid for the explosion limit (*cf.* page 294):

$$p_{H_2}p_{O_2} = \text{const} \quad (3)$$

This relation is in general confirmed by experiment, although, to be sure, with systematic variations that could really be expected, since in (3) the impact cross sections of  $H_2$  and  $O_2$  influencing the diffusion coefficient have not been taken into account, nor has it been considered that, at variously great absorption of  $H_2$  and  $O_2$  at the wall, the breaking probability can have changed. In a tube with a diameter of 1.8 cm at  $550^\circ$ , Hinshelwood found the values of  $p_{H_2}$ ,  $p_{O_2}$  and their products at the lower explosion limit as they are given in Table 50.

Addition of inert gases lowers the lower explosion limit in the same way and according to the same formal law, as we have seen in phosphorus oxidation. At the limit, the following is valid:

$$d^2[H_2][O_2] \left\{ 1 + \frac{a[A]}{[H_2] + [O_2]} \right\} = \text{const}$$

If the pressures are measured in mm Hg, the constant is  $\sim 10$  for  $550^\circ C$ .

Argon, corresponding to its greater impact cross section, reduces the explosion limit of  $H_2 + O_2$  more than helium, as can be seen from Table 51.

Tauzin<sup>1</sup> has made very careful studies of the explosion limits, especially for reaction containers of various sizes, for various gas mixtures, and in the presence of various amounts of inert gases. Tauzin also points out the fact that, in determining ignition temperatures at atmospheric pressure, mistakes are often made because the gas is introduced into an evacuated, hot reaction container and ignition can actually take place while the gas is passing through the low-pressure explosion range.

**2. The Upper Explosion Limit.**—The general position of the upper explosion limit for oxygen-hydrogen is clear from Fig. 162, page 293. The pressures above which explosion does not take place amount in order of magnitude to 100 mm Hg. Since the influence of the wall does not come

<sup>1</sup> TAUZIN, P., *Ann. phys.*, (11), **6**, 575 (1936).

TABLE 52.—UPPER EXPLOSION LIMIT FOR  $H_2 + O_2$  (FROM HINSHELWOOD AND GRANT)<sup>1</sup>

| $t^\circ C$ | Aluminum<br>container           | Quartz<br>container |
|-------------|---------------------------------|---------------------|
|             | Upper explosion<br>limit, mm Hg |                     |
| 579         | 187                             | —                   |
| 565         | 135                             | 158.5               |
| 550         | 101                             | 120                 |
| 535         | 77                              | 88                  |
| 520         | 58.5                            | —                   |
| 518         | —                               | 64                  |
| 500         | 37.5                            | 44                  |

<sup>1</sup> GRANT, G.H., and C.N. HINSHELWOOD, *Proc. Roy. Soc. London, A*, **138**, 29 (1933).

into consideration, the values are easier to reproduce than those for the lower limit; *cf.* Table 52.

The position of the upper limit is, as in other cases, conditioned by deactivation in the gas phase, and this deactivation, according to Hinshelwood,<sup>1</sup> is due to a triple collision process in the gas phase. The formal presentation by Hinshelwood has been attacked, to be sure, but it can be modified in such a manner that all the essential facts can be accounted for while the relations found by Hinshelwood are nevertheless retained.<sup>2</sup> Hinshelwood's (not entirely acceptable) derivation of the limit is as follows (*cf.* in this connection pages 323*ff.*). Let  $X$  and  $Y$  be two kinds of particles (let us say, atoms and free radicals) at whose collision chain-branching can take place, insofar as the impact of a third molecule does not prevent this (in which manner is not stated). If  $\nu$  is the probability of branching in a collision of  $X$  and  $Y$  and if  $Z_{H_2}$ ,  $Z_{O_2}$ , and  $Z_M$  are the impact numbers of  $H_2$ ,  $O_2$ , and compounded inert gas  $M$  with the collision complex  $XY$ , then the condition should read: Branching number equals deactivation number

$$\nu k[X][Y] = Z_{H_2}[X][Y][H_2] + Z_{O_2}[X][Y][O_2] + Z_M[X][Y][M] \quad (4)$$

or, from this,

$$\nu k = Z_{H_2}[H_2] + Z_{O_2}[O_2] + Z_M[M] \quad (5)$$

This is in accord with the empirically determined explosion limit within the limits of error, if  $\nu$ , the branching probability, is assumed to be propor-

<sup>1</sup> GRANT, G.H., and C.N. HINSHELWOOD, *Proc. Roy. Soc. London, A*, **141**, 29 (1933). *Cf.* also HINSHELWOOD and WILLIAMSON, quoted p. 290.

<sup>2</sup> *Cf.* KASSEL, L.S., and H.H. STORCH, *J. Am. Chem. Soc.*, **57**, 672 (1935). KASSEL, L.S., *Chem. Rev.*, **21**, 331 (1937). LEWIS, B., and G. v. ELBE, *J. Am. Chem. Soc.*, **59**, 656 (1937); as well as "Combustion, Flames and Explosions of Gases." Further, JOST, W., and L. v. MÜFFLING, *Z. physik. Chem., Sec. A*, **183**, 43 (1938).

tional to  $e^{-E/RT}$ , where  $E \sim 24$  to  $26$  kcal (cf. page 298). The derivation (and the conception underlying it) is incorrect to the extent that in reality no chain break has been introduced (cf. pages 327ff.). The effectiveness of  $H_2$  and  $O_2$  is found to be about proportional to their number of impacts. For  $Z_{H_2}/Z_{O_2}$ , Hinshelwood computes  $\sim 0.34$ , and  $\sim 0.33$  is found for  $Z_{H_2}/Z_{O_2}$  from the empirical relation

$$P_{H_2} = \text{const} - 0.33P_{O_2}$$

which gives the position of the limit for various mixtures (without inert gas). We shall have to be cautious, to be sure, in concluding that this agreement proves the correctness of the underlying idea; for, besides the impact number, in deactivation in a triple collision the specific effectiveness of the individual gas and perhaps the probability of an energy absorption in the impact will play a role, and this could again completely destroy the agreement that had been found.

For similar reasons, the change of the position of the explosion limit found by Frost and Alyea<sup>1</sup> as well as by Hinshelwood, Williamson, and Wolfenden<sup>2</sup> cannot be considered as absolute proof for the underlying idea, nor can the change of the reaction velocity above this limit be so considered when  $H_2$  is replaced by  $D_2$ . These investigators found the following: The upper limit, when  $D_2$  is substituted for  $H_2$ , is moved in the direction of higher pressures, and thus the explosion range is widened in a manner that can be computed in advance from the difference of the impact numbers for  $H_2$  or  $D_2$  as triple collision partners ( $\sim$  as  $1:1/\sqrt{2}$ ). Correspondingly, the velocity above the upper limit is reduced by about  $1/\sqrt{2}$  of the value for  $H_2$ . The results could be understood only if the changed impact number appeared at a single location while all the rest of the impact numbers and activation heats remained unchanged. It is therefore probable that chance compensations of individual entities play a role, a fact that naturally reduces the value of the experiments as proof.

Experiments on the influence of surfaces on ignition within the range of explosion are of basic importance. At normal pressures ( $\sim 1$  atm), two crossed currents of  $H_2$  and  $O_2$  heated to  $560^\circ\text{C}$  or above ignite even without the presence of a surface (Goldmann<sup>3</sup>). If the gases meet at  $520^\circ$ , however, and at pressures that are low but still within the range of explosion ( $\sim 20$  to  $100$  mm), no ignition takes place without a wall (Haber and Alyea).<sup>4</sup> If a quartz rod (or one of glass, porcelain, copper,

<sup>1</sup> FROST, A.A., and H.N. ALYEA, *J. Am. Chem. Soc.*, **56**, 1251 (1934).

<sup>2</sup> HINSHELWOOD, C.N., A.T. WILLIAMSON, and J.H. WOLFENDEN, *Nature*, **133**, 836 (1934).

<sup>3</sup> GOLDMANN, F., *Z. physik. Chem., Sec. B*, **5**, 316 (1929).

<sup>4</sup> HABER, F., and H.N. ALYEA, *Z. physik. Chem., Sec. B*, **10**, 193 (1930). ALYEA, H.N., *J. Am. Chem. Soc.*, **53**, 1324 (1931).

or iron) that has been heated to the same temperature is introduced at the point of crossing, then ignition takes place, although not with a surface consisting of aluminum. [An objection that can be raised to these experiments is mentioned by Hinshelwood and Williamson: The explosion requires a certain time for its development even within the range of explosion, as is generally to be expected theoretically and has also been demonstrated directly by Kowalsky (*cf.* page 305), and this time might be sufficient in the experiments with crossed gas currents. Contrasted with this, it can be said that it would not then be possible to understand at all how ignition takes place with the quartz rod.] The usual explanation for these experiments is therefore to be preferred: In the explosion condition, the number of the initial centers does not, to be sure, appear; for, by means of chain-branching, an explosion can develop from almost any small number of originally present centers. If no centers are present at all, however, the system is in a metastable condition,<sup>1</sup> which can be abolished by introducing a few initial centers. In a system that is left to itself sufficiently long, such centers would of course finally form even without the influence of the wall. The above experiments lead to the conclusion, then, that at least under certain experimental conditions the reaction chains go out from the wall. If the reaction velocity is inhibited by walls of various kinds, *e.g.*, by coating the wall with KCl (Pease<sup>2</sup>), an influence on the chain induction and not only on chain-breaking could be of importance, a fact that Lewis and v. Elbe,<sup>3</sup> among others, pointed out.

Hinshelwood<sup>4</sup> and his collaborators also found a definite inhibition of low-pressure explosions by means of water vapor; *e.g.*, 10 mm H<sub>2</sub>O suppresses it completely. Water vapor also inhibits the wall reaction at low temperatures. We therefore do justice to all the experiments if we assume that at low temperatures, to  $\sim 540^\circ$ , the chains proceed from the wall, whereas at higher temperatures the induction in the gas phase predominates more and more. This also probably explains the observations that yielded a difference in the critical explosion pressures at the upper limit, according to whether H<sub>2</sub> or O<sub>2</sub> was first introduced into the reaction chamber.

The position of the upper explosion limit is—in addition to the effect of inert gases already discussed—considerably influenced by various additions capable of inducing or breaking chains. Nitrogen dioxide, for instance, added in small quantities ( $\frac{1}{100}$  per cent) effects

<sup>1</sup> HADMAN, THOMPSON, and C.N. HINSHELWOOD, *Proc. Roy. Soc. London, A*, **138**, 297 (1932).

<sup>2</sup> PEASE, R.N., *J. Am. Chem. Soc.*, **52**, 5106 (1930).

<sup>3</sup> LEWIS, B., and G. v. ELBE, *J. Am. Chem. Soc.*, **59**, 656 (1937).

<sup>4</sup> GARSTANG, W.L., and C.N. HINSHELWOOD, *Proc. Roy. Soc. London, A*, **130**, 646 (1931).

a widening of the explosion limits. Dixon had already noted this. Systematic experiments of a more recent date are those of Hinshelwood,<sup>1</sup> as well as Norrish<sup>2</sup> and their associates. According to them, small additions of NO<sub>2</sub> have a favorable effect on explosion. In an experiment by Hinshelwood, for example, in which 200 mm H<sub>2</sub> and 100 mm O<sub>2</sub> had reached 400° (in other words, below the lowest explosion temperature, which was about 440°), these gases ignited when only 0.083 mm NO<sub>2</sub> was added, whereas a very slow reaction resulted with an addition of only 0.076 mm. Larger additions of NO<sub>2</sub> have the reversed effect; they retard explosion. It is therefore necessary to attribute to NO<sub>2</sub> both chain-inducing and chain-breaking properties. We shall come back to this question when discussing the reaction mechanism (page 329).

A decidedly inhibiting effect is produced by the addition of halides.<sup>3</sup> Bromine and iodine can suppress low-pressure explosion in concentrations of ~ 1 per hundred, whereas chlorine is less effective. Atomic oxygen or hydrogen aids explosion considerably, which is to be expected but nevertheless requires special discussion, since the concentration of the initial centers does not appear in the formal explosion condition, according to Semenoff (however, cf. page 280). Haber and Oppenheimer<sup>4</sup> were able to ignite oxygen-hydrogen at temperatures below the upper explosion limit if they mixed it with atomic hydrogen that was produced by a spark in hydrogen atmosphere. The partial pressure of the atomic H in 100 mm H<sub>2</sub> was about  $2.5 \cdot 10^{-4}$  mm. Their experiments are reproduced in Fig. 163, according to Semenoff. With increasing pressure, the ignition temperature is constantly reduced till below 300°C, and an upper explosion limit is no longer observed. Semenoff ("Chemical Kinetics and Chain Reactions") raises the objection that, in the experiments of Haber and Oppenheimer, the content of atomic hydrogen was probably approximately proportional to that of molecular hydrogen, since it was produced by spark conduction through the hydrogen. It could therefore be suspected that, if the H-atom concentration were kept constant, an explosion limit would be found, as is indicated by the dashed line in Fig. 163. Semenoff and his associates<sup>5</sup> undertook an investigation of the situation by attempting to keep the H-atom concentration constant. They therefore proceeded in the following manner:

<sup>1</sup> GIBSON, C.H., and C.N. HINSHELWOOD, *Trans. Faraday Soc.*, **24**, 559 (1928). THOMPSON, H.W., and C.N. HINSHELWOOD, *Proc. Roy. Soc. London, A*, **122**, 610 (1929); **124**, 219 (1929).

<sup>2</sup> GRIFFITHS and R.G.W. NORRISH, *Proc. Roy. Soc. London, A*, **137**, 147 (1933).

<sup>3</sup> GARSTANG and C.N. HINSHELWOOD, *Proc. Roy. Soc. London, A*, **130**, 640 (1931); *Z. physik. Chem.*, 1931, Bodenstein-Festband, p. 656.

<sup>4</sup> HABER, F., and F. OPPENHEIMER, *Z. physik. Chem., Sec. B*, **16**, 443 (1932).

<sup>5</sup> DUBOWITSKY, F., A. NALBANDJAN, and N. SEMENOFF, *Trans. Faraday Soc.*, **29**, 606 (1933).



In a detonation tube, the middle portion of which was heated, atomic hydrogen was produced in a concentration of  $\sim 60$  per cent at a constant  $H_2$  pressure of  $\sim 0.1$  mm. Then the discharge was switched off and an oxygen-hydrogen mixture of predetermined pressure was introduced suddenly, and it was noted at what temperatures and pressures explosion took place. The results confirmed the expectations. An explosion range of the same form as without atomic hydrogen was obtained but with considerably widened limits. Then a series of experiments was performed with various current intensities in the tube for producing

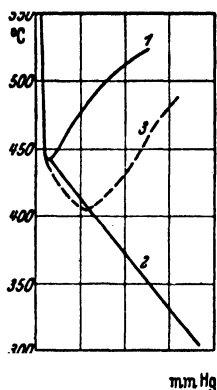


FIG. 163.—1. Normal explosion range of  $2H_2 + O_2$ . (From Haber and Oppenheimer.) 2. The same in the presence of H-atoms. 3. Probable course with constant H-atom concentration. (From Semenov, p. 294.)

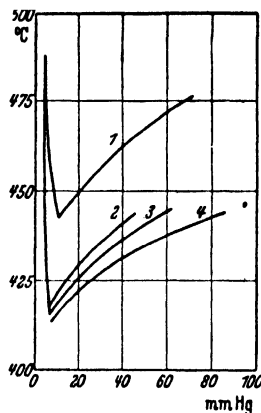


FIG. 164.—1. Explosion range for  $2H_2 + O_2$ , without atomic hydrogen. 2. With atomic hydrogen from a discharge of 0.25 amp. 3. 0.35 amp. 4. 0.5 amp. (From Dubowitzky, Nalbandjan and Semenov.<sup>1</sup>)

atomic hydrogen, and, as expected, it was found that the limits were widened as the intensity of the current increased. The results are given in Fig. 164, according to Semenov. It should be noted that an upper explosion limit exists even at the highest current intensity.

The effect of oxygen atoms is still more decided. Nalbandjan<sup>2</sup> (like Haber and Oppenheimer in the case of atomic hydrogen) found no upper explosion limit at all in this case.

Photochemically, oxygen-hydrogen explosion could be induced by an addition of 0.6 per cent of  $NH_3$  and by illumination with ultraviolet light (Haber, Farkas, and Harteck<sup>3</sup>). Probably the atomic hydrogen formed by this process is responsible for inducing the explosion. Salley and Taylor<sup>4</sup> found, to be sure, that the  $NH_3$ -sensitized light reaction of

<sup>1</sup> DUBOWITZKY, F., A. NALBANDJAN, and N. SEMENOFF, *Trans. Faraday Soc.*, **29**, 606 (1933).

<sup>2</sup> NALBANDJAN, A., *Phys. Z. Sovet*, **4**, 747 (1933).

<sup>3</sup> HABER, F., FARKAS, and P. HARTECK, *Naturwissenschaften*, **18**, 266 (1930).

<sup>4</sup> TAYLOR, H.S., and D.J. SALLEY, *J. Am. Chem. Soc.*, **55**, 96 (1933).

$\text{H}_2 + \text{O}_2$  takes a different course from the Hg-sensitized reaction, and they concluded from this that, in the presence of ammonia, the H-atoms are not alone responsible. How correct this conclusion is must for the time being remain an open question. In the  $\text{NH}_3$ -sensitized photo-reaction, explosion takes place after induction periods of from 30 to 40 sec after illumination, insofar as the pressure is over 300 mm and the temperature over  $415^\circ\text{C}$ . The explosion of oxygen-hydrogen can be induced by ammonia also without illumination.<sup>1</sup> If 1 to 2 mm of  $\text{NH}_3$  are added to oxygen-hydrogen at  $500^\circ$ , an accelerated reaction that results in explosion takes place after several minutes.

A remarkable observation was made by Haber, Farkas, and Harteck.<sup>2</sup> At 300 mm pressure, the ignition temperature is about  $550^\circ$ . If, how-

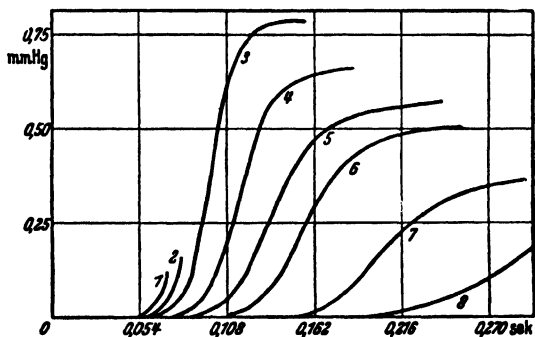


FIG. 165.—Reaction of  $2\text{H}_2 + \text{O}_2$  at  $485^\circ\text{C}$  (pressure changes as a measure of conversion), at initial pressures of (1) 8.2 mm, (2) 7.8 mm, (3) 7.4 mm, (4) 7.1 mm, (5) 6.8 mm, (6) 6.4 mm, (7) 6.1 mm, (8) 5.8 mm. (From Kowalsky.)

ever, an explosion is induced in such a mixture at  $420^\circ$  by means of a spark, and if the chamber is pumped out and is again filled with oxygen-hydrogen at the same pressure, spontaneous explosion takes place at  $420^\circ$ , although several minutes have elapsed between the two explosions.

The time development of the reaction below the lower explosion limit and in the explosion range has been studied by Kowalsky<sup>3</sup> by means of pressure recordings with a sensitive manometer. In Fig. 165, a number of curves are reproduced from Semenoff. They show the conversion in time (expressed by pressure rise) for a series of oxygen-hydrogen mixtures at pressures above the lower explosion limit. The explosion limit at the experimental temperature of  $485^\circ\text{C}$  is found to be at 4.5 mm. The pressure range extends from 5.8 to 8.2 mm. For the initial stage, the relation derived by Semenoff holds:  $\Delta p \sim e^{kt}$ .

<sup>1</sup> HINSHELWOOD, C.N., and A.T. WILLIAMSON, quoted p. 292. WILLIAMSON, A.T., and PICKLES, *Trans. Faraday Soc.*, **30**, 926 (1934).

<sup>2</sup> HABER, F., FARKAS, and P. HARTECK, *Z. Elektrochem.*, **36**, 711 (1930).

<sup>3</sup> KOWALSKY, A., *Phys. Z. Sowet*, **1**, 595 (1932); **4**, 723 (1933).

Induction periods for oxygen-hydrogen ignition in the neighborhood of the explosion limits and in the interior of the explosion range have been measured by Stern, Kravetz, and Sokolik.<sup>1</sup> The remarkable result of these investigations is that the induction period within the explosion range is independent of the temperature.

Tauzin<sup>2</sup> has attempted to determine by means of photographic recording of the spread of the flame in low-pressure explosions whether ignition proceeds from the wall or not. The recordings show practically simultaneous ignition in the entire volume. If it were assumed that ignition began at the wall, a velocity of  $\geq \sim 1000$  m/sec would have to be assumed for its spread.

Tauzin also gives very careful results for the position of the upper explosion limit for greatly varying experimental conditions.

For experiments on the third explosion limit of oxygen-hydrogen that probably represent the transition to purely chemical ignition, although chain-branching might play a role, see Oldenberg.<sup>3</sup>

**3. Reaction outside the Explosion Limits.**—Above the upper explosion limit, the reaction is at first quite slow and clearly a wall reaction to a considerable extent. To be sure, the reaction in immediate proximity to the upper limit has hardly been investigated. At 550°C, the upper limit is at about 100 mm Hg. At 540°, the reaction between 50 mm O<sub>2</sub> and 100 mm H<sub>2</sub> in a quartz chamber  $\sim 250$  cm<sup>3</sup> in volume was observed from the change in pressure by Hinshelwood<sup>4</sup> and his associates. Here the reaction velocity is very small. The reaction is of a high order and in addition rises with the temperature till about the fourth order. In a porcelain chamber at 569°, the reaction was about of the third order with respect to hydrogen and between the first and second order with respect to oxygen. In a quartz chamber, the velocity at 549° was somewhat more than proportional to the square of the H<sub>2</sub> concentration and the first power of the O<sub>2</sub> concentration. The reaction takes an auto-catalytic course, the velocity increases to the extent that water vapor increases, and the surface reaction at low temperatures is inhibited by water vapor. The auto-catalytic reaction above the upper explosion limit has been studied recently in greater detail by Chirkov.<sup>5</sup> He worked with a reaction chamber of Durobax glass with a diameter of 5 cm and 200 to 260 cm<sup>3</sup> of volume. In an experiment that was conducted at 550 mm initial pressure and 524°C, the reaction velocity, determined

<sup>1</sup> STERN, W., B. KRAVETZ, and A. SOKOLIK, *Acta Physicochim. URSS*, **8**, 461 (1938).

<sup>2</sup> TAUZIN, P., quoted p. 299.

<sup>3</sup> OLDENBERG, O., and H.S. SOMMERS, *J. Chem. Phys.*, **7**, 279 (1939).

<sup>4</sup> HINSHELWOOD and WILLIAMSON, quoted p. 292. HINSHELWOOD and THOMPSON, *Proc. Roy. Soc. London, A*, **118**, 170 (1928). GIBSON and HINSHELWOOD, *Proc. Roy. Soc. London, A*, **119**, 591 (1928).

<sup>5</sup> CHIRKOV, N., *Acta Physicochim. URSS*, **6**, 915 (1937).

from the decrease in pressure, showed the typical auto-catalytic course (Fig. 166a). The reaction velocity  $w$  can be given by the following

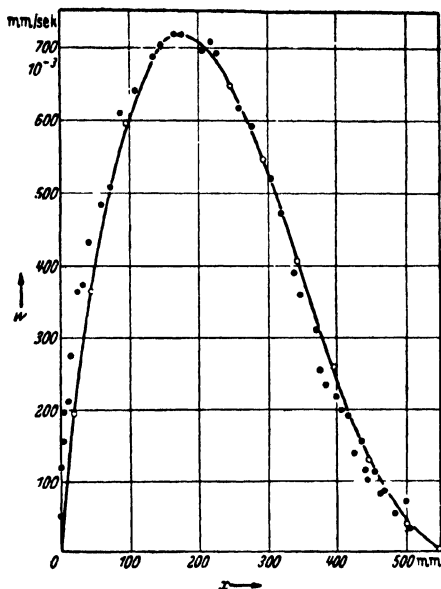


FIG. 166a. Reaction velocity  $w$  of  $2\text{H}_2 + \text{O}_2$  at an initial pressure of 550 mm and at  $524^\circ\text{C}$ , as the function of the quantity of water formed  $x$ . (From Chirkov.<sup>1</sup>)

equation if  $p$  is the initial pressure and  $x$  the converted mass (= amount of water formed):

$$w = kx(p - x)^2 \quad (6)$$

At  $524^\circ\text{C}$ , for example,  $k = 2.9 \cdot 10^{-8}$ , if  $p$  and  $x$  are expressed in mm Hg and the time in seconds. At constant temperatures,  $k$  is constant. An experiment conducted at  $493^\circ\text{C}$  and 402 mm pressure with an addition of 130 mm of water vapor is very illuminating. In Fig. 166b, the result of this experiment is graphically presented. In addition, the reaction velocity is plotted that would result according to (6) in an experiment in which the added water was present as  $2\text{H}_2 + \text{O}_2$ . Essentially, the reaction velocity found with the addition of water corresponds to the values computed

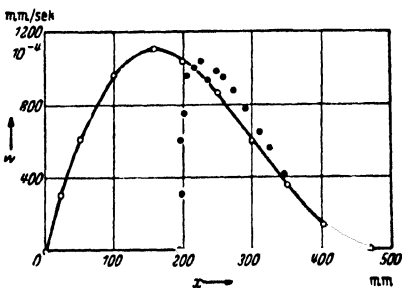


FIG. 166b.—Reaction of  $2\text{H}_2 + \text{O}_2$  with added water vapor—●—○—velocity variations which would have resulted if the water had been present as  $2\text{H}_2 + \text{O}_2$ . (From Chirkov.<sup>1</sup>)

<sup>1</sup> CHIRKOV, N., *Acta Physicochim.*, 6, 915 (1937).

for the point of time when exactly the same quantity of water has been formed in the course of the reaction. This quantity is not accepted immediately, however, but rather after a certain induction period which is short compared with the time that is generally necessary for the auto-catalytic start of the reaction, namely,  $\sim 170$  sec. The temperature dependence of the reaction velocity corresponds to an apparent activation heat of  $\sim 75$  kcal.

The above equation is not valid for all mixtures. At low hydrogen partial pressures, the time law analogous to (6) is, to be sure, still found to hold

$$w = kx(p - x)^2 \quad (7)$$

where  $p$ , however, is now the initial partial pressure of the hydrogen

TABLE 53.—200 MM  $H_2$  + 100 MM  $O_2$  AT  $559^\circ C$

| $N_2$ | Velocity (Relative) |
|-------|---------------------|
| 0     | 1                   |
| 100   | 2.23                |
| 200   | 3.64                |
| 300   | 4.61                |
| 500   | 10.4                |

and  $x$  its decrease (= water formed); hence

$$w = k' [H_2O][H_2]^2$$

Here  $k'$  is not constant in mixtures with a great deal of oxygen but is rather given by

$$k' = K \left\{ \frac{[O_2]}{[H_2]} \right\}_{\text{initial}}$$

Hinshelwood<sup>1</sup> points out that the effect of water vapor does not always have a specific chemical cause but rather that added inert gases likewise accelerate reaction. The influence of inert gas does not always proceed linearly with the pressure, but it can be represented sufficiently exactly by a linear relation up to 400 mm. The effectiveness of various additions is, according to Hinshelwood, given in the following ratio:

$$He:N_2:A:H_2O = 1:3:4:5 \quad (8)$$

The addition of nitrogen is just about as effective as a corresponding increase of the  $O_2$  concentration. In an experiment, the following was obtained (*cf.* Table 53), for instance.

An explanation of the water effect as an analogous inert gas influence would mean that  $H_2O$  as an inert gas must be much more effective than

<sup>1</sup> HINSHELWOOD and WILLIAMSON, quoted p. 292. The experiments of Chirkov are, however, not to be interpreted in this way. *Cf.* Prettre's experiments on the condition of the wall, pp. 310ff.

the reaction partners themselves. Even with this, however, the findings of Chirkov could hardly be explained. A decision on the  $H_2O$  effect does not seem possible without further experiments. Probably a special wall influence plays a role in Chirkov's case, and this seems almost certainly indicated by the experiments of Prettre discussed below (pages 366ff.).

The influence of inert gas apparently rests on an inhibition of the diffusion of chain agents to the wall. This is proved by Hinshelwood's experiments with packed and unpacked chambers as well as by variation of the diameter of the chamber. The reaction velocity in an empty quartz chamber of 301 cm<sup>3</sup> volume and 256 cm<sup>2</sup> surface, and that in a corresponding chamber that was packed with 17 quartz tubes 1 cm in diameter, so that it had a free volume of 230 cm<sup>3</sup> and a surface of 1245 cm<sup>2</sup>, were in the ratio of 17.9:1, with stoichiometric oxygen-hydrogen at 550°C and 600 mm in the ratio 12.6:1; and at 300 mm.

In changing the diameter of the chamber, it is difficult to obtain reliable quantitative values, since the nature of the wall is generally simultaneously changed. If this element of uncertainty is taken into account, the experiments of Hinshelwood and his associates yield a fairly good proportionality with the square of the diameter, as could be expected in the case of a chain reaction with chain-breaking at the wall. In a mixture of  $2H_2 + O_2$  at 560°C and initial pressures of 600 and 300 mm, the velocities were observed as shown in Table 54. A velocity

TABLE 54

| Diameter of the container, mm.....  | 17     | 32     | 56     | 77     |
|-------------------------------------|--------|--------|--------|--------|
| Velocity $w$ at $p_0 = 600$ mm..... | 0.85   | 3.49   | 9.35   | 33.8   |
| Velocity $w$ at $p_0 = 300$ mm..... | 0.18   | 0.50   | 0.94   | 3.45   |
| $w_{600}/d^2$ .....                 | 0.0030 | 0.0034 | 0.0030 | 0.0057 |
| $w_{300}/d^2$ .....                 | 0.0006 | 0.0005 | 0.0003 | 0.0006 |

proportional to  $d^2$  which at the same time depends on the presence of inert gases in the manner indicated can easily be derived for a chain reaction with chain-breaking at the wall. Even so, the findings are very peculiar, for we should expect such a reaction with chain-breaking at the wall at the lowest pressures below the lower explosion limit, insofar as a pure wall reaction does not predominate. If the lower limit is then passed and the upper explosion limit is approached, chain-breaking in the gas phase must of course more and more predominate and finally be practically alone determining. At least just above the upper limit, where unfortunately no experiments have been made, we should expect that a gas-phase deactivation would be determining. If, instead, we find that at still higher pressures chain-breaking at the wall deter-

mines the velocity, then this fact is at least very surprising and suggests that an entirely different reaction mechanism is determining above the upper limit from that below and at this limit.

Still another remarkable observation by Hinshelwood and his associates must be mentioned here.<sup>1</sup> In a silver chamber, the reaction of a high order usually observed between 540° and 600° is almost wholly suppressed. Added gases are without any influence, nor can the reaction be induced by introducing a quartz rod into the reaction chamber. Thus contradictions result if we assume either that the silver tends greatly to break chains or that it does not induce chains. In experiments with flowing oxygen-hydrogen ( $2\text{H}_2 + \text{O}_2$ ) at 520° to 550°C, Pease<sup>2</sup> found the reaction very sensitive to the nature of the surface. The reaction velocity was the greatest when the reaction chamber had been washed with nitric acid and rinsed with distilled water. On the other hand, the reaction velocity was considerably decreased when the chamber was washed out with a potassium chloride solution. In the chambers treated with nitric acid, up to one molecule of  $\text{H}_2\text{O}_2$  was found to four molecules of water formed; whereas, in the chambers coated with KCl, no peroxide appeared. According to unpublished experiments of Hinshelwood's, such an effect of KCl was not observable under the conditions of most of his experiments in quartz chambers.<sup>3</sup> According to Lewis and v. Elbe (quoted page 300), this is supported by the fact that KCl inhibits the reaction under conditions in which the chain induction takes place at the wall but not under conditions in which the chains begin in the gas phase. Moreover, KCl destroys peroxidic substances.

Important disclosures on the effect of the wall above the upper explosion limit have been furnished by experiments by Prettre.<sup>4</sup> Between 540° and 580°C at pressures between 300 and 700 mm Hg in a pyrex chamber coated with KCl, he found a velocity equation

$$w = k[\text{H}_2]^2[\text{O}_2]pe^{-95,000/RT}$$

which differentiates itself from the expression of the third order found by Bodenstein (quoted page 289) for heterogeneous reactions only by the additional factor  $p$ . The reaction can proceed fifty times more slowly than without KCl coating. Figure 167 shows the reaction velocities found in experiments with pure pyrex glass as well as with walls coated with KCl. The reaction chamber had a diameter of 6 cm and was 12 cm in length. The experiments were carried out at about 550° with a mixture of  $2\text{H}_2 + \text{O}_2$  at the following pressures:

<sup>1</sup> MOELWYN-HUGHES, ROLFE, and HINSHELWOOD, *Proc. Roy. Soc. London, A*, **139**, 521 (1933). See also HINSHELWOOD and WILLIAMSON, quoted p. 294.

<sup>2</sup> PEASE, R.N., *J. Am. Chem. Soc.*, **52**, 5106 (1930).

<sup>3</sup> HINSHELWOOD and WILLIAMSON, quoted p. 294.

<sup>4</sup> PRETTRE, M., *J. chim. phys.*, **33**, 189 (1936); *Compt. rend.*, **201**, 728, 962 (1935).

|                  | Without KCl |     |     | With KCl |     |     |     |     |     |
|------------------|-------------|-----|-----|----------|-----|-----|-----|-----|-----|
| Test number..... | 5           | 4   | 9   | 10       | 3   | 36  | 37  | 41  | 38  |
| p, mm Hg.....    | 636         | 546 | 418 | 625      | 371 | 648 | 533 | 423 | 328 |

Reproducible measurements can be obtained only if the absorbed gases (water vapor and hydrogen) are removed between experiments by careful pumping. For walls coated with KCl, 15 to 20 hr of pumping after rinsing with oxygen are necessary. For uncoated glass walls, this does not suffice, since such walls tenaciously hold considerable quantities of  $\text{H}_2\text{O}$  and  $\text{H}_2$ . For pure glass walls, the curves often show an auto-

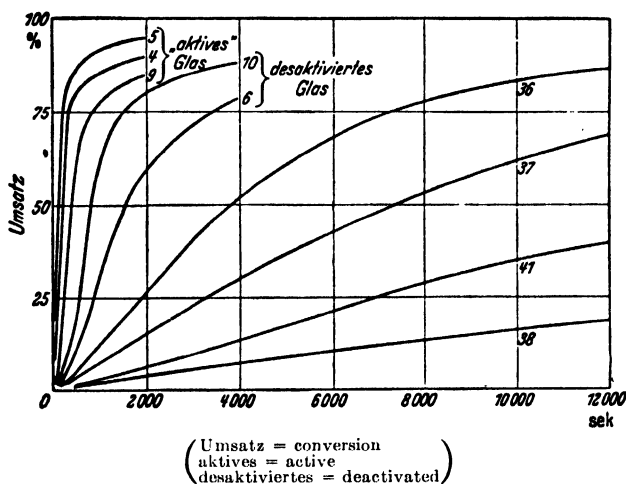


FIG. 167.—Reaction of  $2\text{H}_2 + \text{O}_2$  in Pyrex glass with and without KCl coating at  $550^\circ\text{C}$ . Compare the text. (From Prettre, p. 306.)

catalytic character (as in Chirkov's experiments, page 307). For walls coated with salt, an induction period is always present that is over by the time 10 per cent has reacted. As a velocity expression up to the immediate proximity of the explosion limit (above  $570^\circ$ ), we obtain the equation given above with an apparent activation energy of about 95 kcal. The addition of nitrogen or argon, as in Hinshelwood's experiments, accelerates the reaction considerably, a sign that we are dealing with a gas reaction with chain-breaking at the wall.

Prettre's observations on the condition of the wall as well as on its effect on the reaction are most interesting. Pyrex and quartz glass absorb<sup>1</sup> great quantities of hydrogen between  $450^\circ$  and  $600^\circ\text{C}$ , and after some 10 hr no equilibrium is as yet established. It is clearly a case of

<sup>1</sup> Cf. WILLIAMSON, *J. Am. Chem. Soc.*, **55**, 1437 (1933).



activated absorption<sup>1</sup> since the absorbed quantity increases with the temperature. It increases with the pressure according to a Langmuir isotherm. Prettre determined the absorption velocity of hydrogen to pyrex (a container with a volume of 135 cm<sup>3</sup> and a surface of 2035 cm<sup>2</sup> filled with pieces of glass) (Table 55).

At 580°C, the 2035 cm<sup>2</sup> of surface absorbed over 10 cm<sup>3</sup> of H<sub>2</sub> in 20 hr at a pressure of 400 mm (or to 0° and 760 mm) without reaching equilibrium. That would correspond to a coating of about 100 layers of

TABLE 55.—ADSORPTION VELOCITY OF H<sub>2</sub> TO PYREX AT VARIOUS TEMPERATURES AND PRESSURES BETWEEN 250 AND 350 MM Hg

| Temperature, ° abs .....                           | 813<br>366.3                                   | 832<br>357.4 | 853<br>375.5 |
|--|--|--------------|--------------|
| Initial pressure, mm Hg.....                       |  |              |              |
| Change in pressure<br>(corresponding to 580°C), mm | Time required for this<br>decrease in pressure |              |              |
| 350-340.....                                       | 16'  | 8'           | 3'45"        |
| 350-330.....                                       | 41'  | 21'          | 10'          |
| 350-250.....                                       | 210'   | 108'         | 53'          |
|  | Activation energy, kcal                        |              |              |
| 350-340.....                                       | 49.0   | 50.9         |              |
| 350-330.....                                       | 47.3   | 49.8         |              |
| 350-250.....                                       | 47.0   | 47.8         |              |

molecules. If we do not wish to assume that the effective surface is extraordinarily large, the only possibility that remains is to assume a regular adsorption of the hydrogen with diffusion into the interior of the glass, and this is quite in accord with other experiences.<sup>2</sup> The adsorption velocity is much smaller if the wall is coated with KCl, but it is nevertheless noticeable. Water vapor is likewise vigorously adsorbed between 500° and 600° (by means of special experiments, it was determined that this effect is not produced by the condensation of water vapor outside the hot reaction chamber), and it is adsorbed with a greater velocity than hydrogen. Surfaces coated with KCl also adsorb water vapor, but more slowly.

Oxygen is practically not adsorbed between 500° and 600°C.

The varying adsorption condition is of extraordinary influence on the reaction velocity. Figure 168 shows the results of the velocity measurement in a quartz container (of 149 cm<sup>3</sup> volume, packed with pieces of

<sup>1</sup> TAYLOR, H.S., *J. Am. Chem. Soc.*, **53**, 578 (1931).

<sup>2</sup> For diffusion in solids, cf. W. Jost, "Diffusion und chemische Reaktion in festen Stoffen," Theodor Steinkopff, Dresden, 1937.

quartz with a total surface of 1015 cm<sup>2</sup>). In this case, we are not yet dealing with the pure wall reaction that takes place with essentially denser packing but with much smaller reaction velocity. The experiments are conducted with  $2\text{H}_2 + \text{O}_2$ , 600 mm Hg, and 540°C. The pressure changes are plotted as a measurement of the velocity. Curve 0 refers to the first experiment without previous adsorption of water. The succeeding curves 7, 9, 8, and 5 refer to experiments that were carried out under otherwise equal conditions and in which increasing quantities of water were adsorbed, corresponding to a decrease in pressure

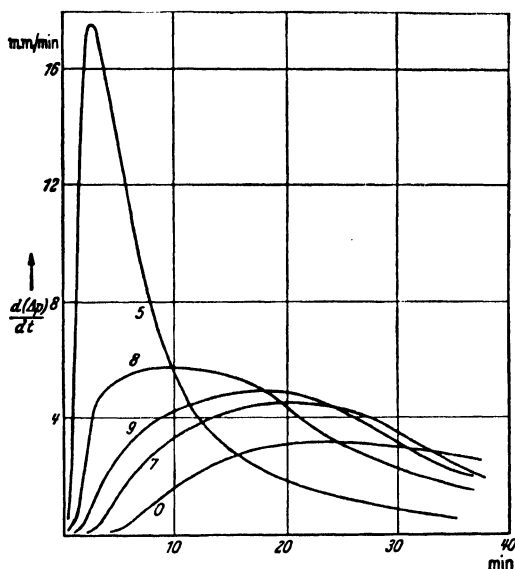


FIG. 168.—Reaction of  $2\text{H}_2 + \text{O}_2$  with 600 mm Hg and 540°C in a packed quartz container, and with various quantities of absorbed water. Compare the text. (From Prettre, p. 306.)

of 5, 9, 23, and 70 mm, respectively. After adsorption, the chamber was rapidly pumped out, whereupon first  $\text{O}_2$  and then  $\text{H}_2$  were introduced for an experiment. Desorption takes place too slowly to make the inert gas effect of desorbed water responsible for the considerable reaction acceleration observed.

Experiments were also carried out with adsorbed  $\text{H}_2$ , but because of the smaller reaction velocity they were made at 550°C (Fig. 169). Experiment 10 was made under conditions similar to those of experiment 0, *i.e.*, with as little adsorption as possible. The following experiments 13, 16, 12, and 14 were made with  $\text{H}_2$  adsorption corresponding to a decrease in pressure of 4, 15, 39, and 44 mm Hg. Hydrogen adsorption has exactly the reverse effect of that produced by water vapor; in other words, it has a strong reaction-inhibiting effect, while, remarkably

enough, the induction period is suppressed. In the very first stage, adsorbed  $H_2$  therefore accelerates the reaction. In spite of all this, however, the character of the conversion is preserved as a chain reaction taking place in the gas phase.

Prettre<sup>1</sup> also conducted experiments in an empty pyrex chamber and in one filled with glass tubes, with and without KCl coating of the wall. The volume and the surface in the empty chamber were 265 cm<sup>3</sup> and 281 cm<sup>2</sup>; in the packed chamber, they were 177 cm<sup>3</sup> and 1298 cm<sup>2</sup>. At about 550°C, the coating of the surface with KCl reduced the reaction velocity  $\frac{1}{40}$  up to  $\frac{1}{45}$ ; in the packed chamber (in which the reaction

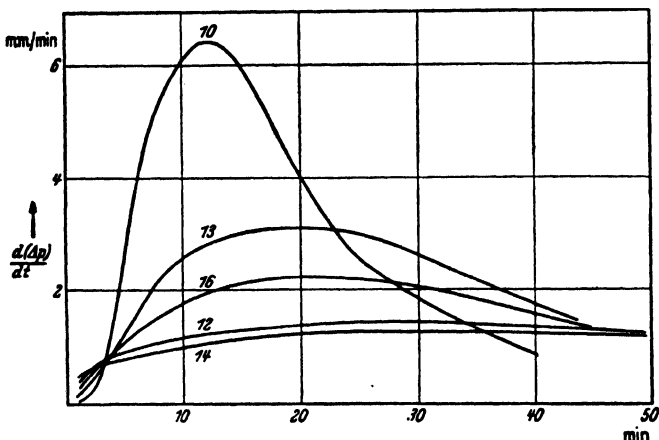


FIG. 169.—Reaction of  $2H_2 + O_2$ , as above; however, in the presence of adsorbed hydrogen at 550°C. (From Prettre.)

velocity was reduced to about  $\frac{1}{20}$  from the start), it reduced it to only about  $\frac{1}{8}$ . Prettre concluded from these results that KCl does not promote chain-breaking at the wall but rather decreases the induction. Considering the findings of Lewis and v. Elbe as well as Kassel and Storch (see page 296), this does not sound convincing. It is unfortunate that the same experiments were not carried out with and without the addition of inert gas. In any case, however, the experiments clearly show the influence of the condition of the wall and that the order in which the gases are introduced into the chamber can be of importance for the reaction.

**4. Experiments with Free Atoms and Radicals.**—The experimental findings in the reaction of  $O_2$  with  $H_2$  on the position of the explosion limits and on the influence of the wall, of inert gases, and of certain additions effective in small quantities, like  $NO_2$  or  $I_2$ , show with certainty that we are dealing with a chain reaction and with explosion by chain-

<sup>1</sup> PRETTRE, M., *Mém. poudres*, **26**, 239 (1935).

branching. In general, the participation of stimulated, energy-rich molecules is less likely in chain reactions than that of free atoms and radicals, for a stimulated molecule again loses its stimulus energy very rapidly by collisions with other molecules. If active particles come into play that possess a longer life (especially if they occur in concentrations that are above those of thermal equilibrium with unstimulated particles) and are preserved by the liberated reaction energy, then almost only free atoms and radicals come into consideration. Their life span is so relatively great because they can disappear only if they collide with another such particle, and because even then a triple collision is generally necessary for their destruction. For these reasons, we are led to assume the participation of atoms and radicals in the reaction. Added to this is the fact that we can prove the presence of OH-radicals in oxygen-hydrogen combustion at higher temperature directly by means of the spectroscope, and that the presence of H-atoms in the flame in concentrations that lie well above those of thermal equilibrium is certain.<sup>1</sup>

It would not be satisfactory, however, simply to assume the participation of the atoms H and O and of the radical OH, to make a list of the double and triple collision reactions that are possible among these particles and with H<sub>2</sub> and O<sub>2</sub>, and then for formal reasons simply to eliminate those which do not fit into the scheme for explaining the observed phenomena. Rather, extensive investigations have been made in the last 15 years on the reactions of free atoms. They have been presented in the most varied manner, and we are therefore in possession of definite facts about many of the partial reactions coming into consideration in oxygen-hydrogen combustion. We shall briefly present these experiences in the succeeding pages, but naturally the space available does not permit a detailed description of the experimental methods.<sup>2</sup>

For all practical purposes, two methods come into consideration: (1) an electrical discharge (H- and O-atoms as well as OH-radicals are produced in this way) and (2) the photochemical disintegration of molecules. In the latter case, the molecule can be disintegrated by radiation that it absorbs itself (in the case of hydrogen and oxygen, for example, which absorb only in the extreme ultraviolet, this has hardly been carried out practically<sup>3</sup>), or another material can be permitted to be absorbed (frequently mercury vapor with its resonance line at 2537 Å) and can then transfer its impulsive energy in an impact of the second kind to

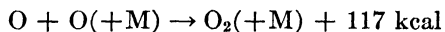
<sup>1</sup> For both these assertions, see K.F. Bonhoeffer, *Z. Elektrochem.*, **42**, 449 (1936).

<sup>2</sup> Cf. in this connection GEIB, K.H., Atom Reactions, *Ergeb. exakt. Naturw.*, **15**, 44 (1936); also "Reaktionen der Wasserstoff- und Sauerstoffatome," *Habilschr.*, Leipzig, 1937.

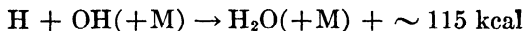
<sup>3</sup> For oxygen, see page 318.

the nonabsorbing molecule and split the latter into atoms (thus H-atoms can be produced by irradiating the Hg resonance line into hydrogen to which some mercury has been added). If the free atoms or radicals are produced in a discharge, we are generally forced to work at quite low pressures ( $\sim 1$  mm Hg or below); but, to compensate for it, we can achieve very high relative atom concentrations, close to 100 per cent in the case of H. The gases that enter into reaction with the atoms or radicals pumped off from the discharge must then be added to them at correspondingly low pressures.

a. *The Reaction*  $\text{H} + \text{H}(+\text{M}) \rightarrow \text{H}_2(+\text{M}) + 102.6 \text{ kcal.}$ —The union of H-atoms to  $\text{H}_2$  takes place in the gas phase in a triple collision in which various gases are variously effective as triple collision partners according to their number of impacts and the probability of the energy transfer. The experimental findings of the individual authors still vary considerably. For an estimate according to order of magnitude, the following should suffice: At atmospheric pressure, about every thousandth impact is a triple collision. If H-atoms have been pumped off from a discharge at about  $\frac{1}{1000}$  atm, their impact number is  $\sim 10^6$  per second, the fraction of triple collisions (which is proportional to the pressure)  $\sim 10^{-6}$ ; thus the life span of the H-atoms is  $\sim 1$  sec, during which they have time to diffuse to the wall at these low pressures even in large containers. In addition, atoms are also destroyed at the wall, and this can be imagined in the following manner: An atom is adsorbed at the wall and then remains there until a second atom is added and recombines with it. The wall (glass) is poisoned<sup>1</sup> by water for the recombination<sup>2</sup> of the atoms. The estimate for the recombination in the gas volume and the life span of the free atoms can approximately be transferred to the reaction



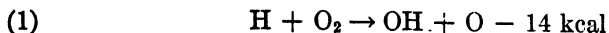
as well as



We shall come back to the latter reaction. The recombination reactions take place without activation heat and therefore depend only slightly on the temperature.

<sup>1</sup> It should be considered that, in auto-catalytic oxygen-hydrogen combination above the upper explosion limit, the poisoning of the wall plays a role for chain-breaking by adsorbed water.

<sup>2</sup> For the production and reaction of atomic hydrogen, cf. the following: BONHOEFFER, K.F., *Ergeb. exakt. Naturw.*, **6**, 201 (1927). AMDUR, *J. Am. Chem. Soc.*, **57**, 856 (1935). SMALLWOOD, *J. Am. Chem. Soc.*, **51**, 1985 (1929); **56**, 1542 (1934). STEINER, W., and Z. BAY, *Z. physik. Chem., Sec. B*, **3**, 149 (1929). BODENSTEIN-FESTBAND, 1931, p. 817. *Trans. Faraday Soc.*, **31**, 623 (1935). AMDUR, *J. Am. Chem. Soc.*, **60**, 2347 (1938).

b. *The Reaction of H with O<sub>2</sub> and H<sub>2</sub> + O<sub>2</sub>.—The reaction*

will certainly take place to a marked extent at higher temperatures and should be considered as a possible chain-branching reaction in oxygen-hydrogen combustion. Unfortunately there are no direct experimental data on this reaction. Since the activation heat in exothermic atomic reactions is generally not very high ( $\sim$  several kcal) and as a result the activation heat of endothermic atomic reactions need be only a little higher than the heat of reaction, an activation heat of the order of magnitude of about 20 kcal could be expected for (1). Geib estimates the activation energy at only 14 kcal, since the reverse reaction  $\text{O} + \text{OH} \rightarrow \text{O}_2 + \text{H}$  probably takes place without activation heat. With an activation energy of 14 kcal, the impact yield of (1) at 800° abs, in other words, in the explosion range of oxygen-hydrogen, would be  $\sim 10^{-4}$ .

In addition to the chain-branching reaction (1), there is certainly also an accumulation reaction in the triple collision



for which there is a series of direct experimental proofs. If atomic hydrogen (either from a discharge or photochemically produced) is permitted to react with oxygen at not too high temperatures, hydrogen superoxide is obtained in considerable concentrations in addition to water with a quantum yield to about 3, in which the quantity of H<sub>2</sub>O<sub>2</sub> can amount to about three times as much as the water formed.<sup>1</sup> According to Marshall,<sup>1</sup> we must assume primarily a formation of HO<sub>2</sub> in order to explain the findings. The same reaction is to be demanded for the inhibition of the photochemical chlorine detonating gas reaction by means of oxygen. It is to be assumed that HO<sub>2</sub> is formed at every triple collision. The heat of reaction of the above can be estimated at about 40 kcal (Bodenstein and Schenk, and Kornfeld<sup>2</sup>). The same reaction may be made responsible also for the inhibition of the photochemical HI disintegration (Bates<sup>1</sup>) and results from the consumption of photochemically produced (sensitized by Hg) H-atoms in the presence of oxygen (Farkas and Sachsse<sup>3</sup>). It is hard, however, to harmonize

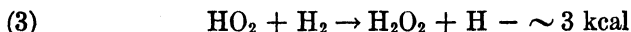
<sup>1</sup> GEIB, quoted p. 315. MARSHALL, A.L., *J. Am. Chem. Soc.*, **49**, 2763 (1927); **54**, 4460 (1932). FRANKENBERGER and H. KLINKHARDT, *Z. physik. Chem.*, Sec. B, **15**, 421 (1932). SALLY and J.R. BATES, *J. Am. Chem. Soc.*, **55**, 110 (1933). BATES, J.R., *J. Am. Chem. Soc.*, **55**, 426 (1933); *J. Chem. Phys.*, **1**, 457 (1933); *Z. physik. Chem.*, Sec. B, **22**, 469 (1933); *Proc. Nat. Acad. Sci. U.S.* **19**, 81 (1933). LAVIN and J.R. BATES, *J. Am. Chem. Soc.*, **55**, 81 (1933). BARAK, M., and H.S. TAYLOR, *Trans. Faraday Soc.*, **28**, 569 (1932).

<sup>2</sup> BODENSTEIN, M., and P.W. SCHENK, *Z. physik. Chem.*, Sec. B, **20**, 420 (1933). KORNFELD, G., *Z. physik. Chem.*, Sec. B, **35**, 236 (1937).

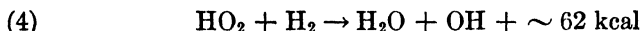
<sup>3</sup> FARKAS, L., and H. SACHSSE, *Z. physik. Chem.*, Sec. B, **27**, 111 (1934).

the quantitative deductions of Farkas and Sachsse with those of other authors. According to them, only about every five hundredth triple collision will lead to  $\text{HO}_2$  formation. It is at any rate certain, however, that  $\text{HO}_2$  is formed in the triple collision.

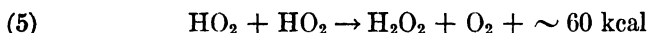
The further reactions according to which  $\text{HO}_2$  could react with  $\text{H}_2$  are



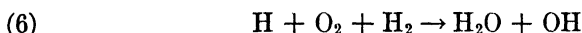
• and



In addition, according to Geib,<sup>1</sup>  $\text{HO}_2$  might be consumed at room temperature chiefly according to the reaction



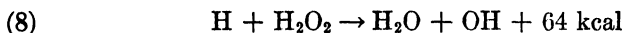
The reaction (3), which first was suggested by Marshall (cited page 317), may be regarded as a possibility after it has been pointed out by Kornfeld (cited page 317) and by Lewis and v. Elbe<sup>2</sup> that apparent difficulties can be overcome. Geib (cited page 315) reports an activation heat of  $\sim 7$  kcal for reaction (4). In any case, it may be assumed that the activation heats of the two reactions (3) and (4) are not very great and that these reactions can play a role at higher temperatures. The reaction proposed by Haber and his associates<sup>3</sup>



is essentially equivalent to the succession of the reactions (2) and (4). Since ozone is formed in flames, the reaction

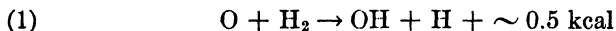


can also play a role under certain circumstances. Its activation heat is, according to Harteck (Geib, cited page 315), probably smaller than 5 kcal. Like ozone,  $\text{H}_2\text{O}_2$  can also be formed in flames, and therefore reaction



can likewise occur, which, according to Geib, takes place with an activation heat of the order of magnitude of 5 kcal.

*c. Reactions of the O-atoms.*—The reaction



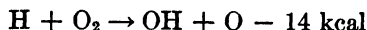
takes place with an activation heat of  $\sim 7 \pm 2$  kcal (Geib), as can be

<sup>1</sup> GEIB, K.H., quoted p. 315; also *Z. physik. Chem.*, Sec. A, **169**, 161 (1934).

<sup>2</sup> LEWIS, B., and G. v. ELBE, *J. Am. Chem. Soc.*, **59**, 656 (1937).

<sup>3</sup> FARKAS, L., F. HABER, and P. HARTECK, *Naturwissenschaften*, **18**, 266 (1930).

concluded from experiments by Harteck<sup>1</sup> and his associates with atomic oxygen<sup>2</sup> from electrical discharge as well as from photochemical experiments.<sup>3</sup> If oxygen atoms are formed in oxygen-hydrogen reaction according to



with chain-branching, they will probably continue to react, again with chain-branching, according to (1), because of the low activation heat.

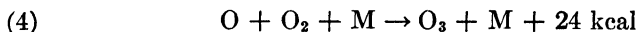
In addition to (1), reactions with smaller activation heats



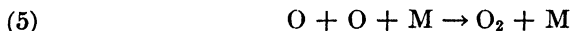
and



can play a role, although, to be sure, only to a very subordinate degree. Ozone formation<sup>4</sup> can also take part according to

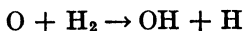


which takes place without activation heat in a triple collision. For the combination of O-atoms, the triple-collision recombination



naturally comes into consideration too. Since, of the active particles H, O, and OH that appear in oxygen-hydrogen combustion, O continues to react with H<sub>2</sub> with the lowest activation heat, its static concentration will in general be smaller than that of H and OH; and the triple-collision recombination (5) will therefore in general give way to the reactions  $\text{H} + \text{H} + \text{M} \rightarrow \text{H}_2 + \text{M}$ ,  $\text{H} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O} + \text{M}$  and probably to the reaction of OH (and also HO<sub>2</sub>) among each other.

In the reaction of oxygen atoms with hydrogen there occurs besides



also the reaction of ozone with hydrogen, the former having been freshly formed from  $\text{O} + \text{O}_2$  in a triple collision and still possessing a part of its formation energy

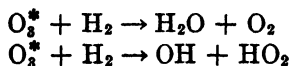
<sup>1</sup> HARTECK, P., and U. KOPSCH, *Z. physik. Chem., Sec. B*, **12**, 327 (1931). HARTECK, P., *Trans. Faraday Soc.*, **30**, 134 (1934).

<sup>2</sup> KISTIAKOWSKY, G.B., *J. Am. Chem. Soc.*, **52**, 1868 (1930). KISTIAKOWSKY, G.B., and SMITH, *J. Am. Chem. Soc.*, **57**, 835 (1935).

<sup>3</sup> This value is probably somewhat too low; in any case, the activation heat of this reaction will be smaller than that of the reaction  $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$ . Cf. GROTH and P. HARTECK, *Z. Elektrochem.*, **44**, 621 (1938).

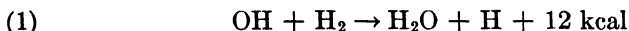
<sup>4</sup> Cf. especially GROTH, W., and P. HARTECK, *Z. Elektrochem.*, **44**, 621 (1938).





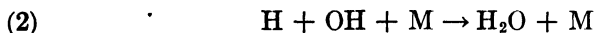
(Groth and Harteck<sup>1</sup>).

*d. Reactions of the OH-radicals.*—The reaction

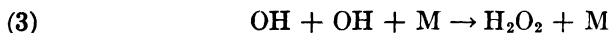


which, according to Geib (cited page 315), takes place with an activation heat of  $\sim 7$  kcal, might be of particular importance in oxygen-hydrogen combustion at higher temperatures.

In addition, the triple-collision recombination



as well as reactions of the OH-radicals among themselves, like



and



which were suggested by Bonhoeffer and Pearson,<sup>2</sup> can come into consideration as chain-breaking (and water forming).

The reaction of OH-radicals that were produced by a discharge in water vapor<sup>2</sup> has been investigated repeatedly in recent times. Spectroscopic methods were employed to determine the OH concentration as well as its change in time (Kondratjew,<sup>3</sup> Oldenberg<sup>4</sup>). Especially Oldenberg was able to achieve high precision by working with a large concave grid. Kondratjew found, first of all, that OH disappears after a reaction of the second order. Since Oldenberg found further that the recombination constant is proportional to the total pressure and also proportional to the pressure of added helium, we must be dealing with a triple-collision reaction for which Frost and Oldenberg assume



which does not contradict Kondratjew's findings, since H and OH originate from H<sub>2</sub>O in equivalent quantity. Nevertheless, Kondratjew believes he can conclude that the process



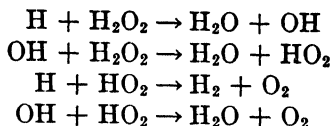
<sup>1</sup> GROTH, W., and P. HARTECK, *Z. Elektrochem.*, **44**, 621 (1938).

<sup>2</sup> BONHOEFFER, K.F., and T.G. PEARSON, *Z. physik. Chem.*, Sec. B, **14**, 1 (1931).

<sup>3</sup> KONDRATJEW, V., and M. ZISKIN, *Acta Physicochim. URSS*, **5**, 301 (1937); **6**, 307 (1937). KONDRATJEW, V., *Acta Physicochim. URSS*, **8**, 315 (1938).

<sup>4</sup> OLDENBERG, O., and A.A. FROST, *J. Chem. Phys.*, **4**, 642 (1936). OLDENBERG, O., and F.F. RIEKE, *J. Chem. Phys.*, **6**, 779 (1938).

is preferred. Since the reactions



would have to follow it and they destroy  $\text{H}_2\text{O}_2$ , there are no contradictions to the empirical findings<sup>1</sup> that no  $\text{H}_2\text{O}_2$  is present. In any case, it can be assumed that OH can recombine either with H or with another OH in a triple collision.

We have discussed the reactions of the H- and O-atoms at some length not only because a knowledge of them is important for explaining the mechanism of the oxygen-hydrogen combustion but also because in part the same reactions also play a role in hydrocarbon combustion and because in part conclusions can be drawn from them in respect to the corresponding reactions of hydrocarbon radicals.

**5. Mechanism of the Oxygen-hydrogen Reaction.**—It has already been mentioned that H-atoms are present in the advanced stage of an oxygen-hydrogen explosion in essentially higher concentrations than correspond to dissociation equilibrium of  $\text{H}_2$ . Goldmann<sup>2</sup> produced oxygen-hydrogen explosions with parahydrogen; at about  $900^\circ\text{C}$ , 50 per cent parahydrogen is, according to Bonhoeffer and Harteck,<sup>3</sup> only partly converted to ordinary hydrogen in 1 sec. However, if a mixture of 74.3 per cent parahydrogen and 25.7 per cent air is ignited, which according to the thermochemical data cannot be heated to more than  $900^\circ\text{C}$ , the parahydrogen is found to be completely converted to normal hydrogen. Since the flame traverses the mixture in a tube with a velocity of  $\sim 1$  m/sec, the mixture would have been at the maximum temperature only  $\sim 10^{-4}$  sec with a burning zone  $\sim 10^{-2}$  cm in width. Thus the H-atom concentration (H-atoms are under these circumstances responsible for the parahydrogen conversion) must have been greater than the equilibrium concentration by an appreciable amount during the explosion. H-atoms therefore are produced in a very high concentration in combustion and certainly play a role in the mechanism. It is known from spectra<sup>4</sup> (see Chap. VII, pages 229ff.) that OH-radicals are present in the flame. All flames of hydrogen or hydrogen-containing compounds show the bands of the radical OH in the ultraviolet, with the strongest bands at  $3064 \text{ \AA}$ . That the OH-radicals play a role in the

<sup>1</sup> BONHOEFFER and PEARSON, quoted p. 320.

<sup>2</sup> GOLDMANN, F., *Z. physik. Chem.*, Sec. B, **5**, 305 (1929).

<sup>3</sup> BONHOEFFER, K.F., and P. HARTECK, *Z. physik. Chem.*, Sec. B, **4**, 129 (1929).

<sup>4</sup> Cf. BONHOEFFER, K.F., and F. HABER, *Z. physik. Chem.*, Sec. A, **137**, 263 (1928).  
BONHOEFFER, *Z. Elektrochem.*, **42**, 449 (1936).

combustion reaction had been suspected early by Bonhoeffer and Haber. The investigations of Kondratjew<sup>1</sup> may be regarded as proof of this. By means of absorption photographs, he determined quantitatively the OH concentration in reacting oxygen-hydrogen and its change with the

TABLE 56.— $\text{H}_2 = 2\text{H} - 102.6 \text{ Kcal}$ 

| $T^\circ \text{ abs}$ | $K_p =$               | % splitting<br>at 1 atm |
|-----------------------|-----------------------|-------------------------|
| 600                   | $3.6 \cdot 10^{-33}$  | $3.0 \cdot 10^{-15}$    |
| 800                   | $1.3 \cdot 10^{-23}$  | $1.7 \cdot 10^{-10}$    |
| 1000                  | $7.0 \cdot 10^{-18}$  | $1.3 \cdot 10^{-7}$     |
| 1200                  | $5.05 \cdot 10^{-14}$ | $1.1 \cdot 10^{-5}$     |
| 1400                  | $2.96 \cdot 10^{-11}$ | $2.9 \cdot 10^{-4}$     |
| 1600                  | $3.59 \cdot 10^{-9}$  | $3.0 \cdot 10^{-3}$     |
| 1800                  | $1.52 \cdot 10^{-7}$  | $1.9 \cdot 10^{-2}$     |
| 2000                  | $3.10 \cdot 10^{-6}$  | $8.8 \cdot 10^{-2}$     |
| 2400                  | $2.89 \cdot 10^{-4}$  | 0.85                    |
| 2800                  | $7.51 \cdot 10^{-3}$  | 4.33                    |
| 3000                  | $2.78 \cdot 10^{-2}$  | 8.31                    |

TABLE 57.— $\text{O}_2 = 2\text{O} - 117.3 \text{ Kcal}$ 

| $T^\circ \text{ abs}$ | $K_p =$              | % splitting<br>at 1 atm |
|-----------------------|----------------------|-------------------------|
| 800                   | $9.2 \cdot 10^{-27}$ | $4.8 \cdot 10^{-12}$    |
| 1200                  | $8.0 \cdot 10^{-16}$ | $1.4 \cdot 10^{-6}$     |
| 1600                  | $2.5 \cdot 10^{-10}$ | $8.0 \cdot 10^{-4}$     |
| 2000                  | $5.2 \cdot 10^{-7}$  | $3.6 \cdot 10^{-2}$     |
| 2400                  | $8.5 \cdot 10^{-5}$  | 0.46                    |
| 2800                  | $3.3 \cdot 10^{-3}$  | 2.86                    |
| 3000                  | $1.4 \cdot 10^{-2}$  | 5.95                    |

TABLE 58.— $\frac{1}{2}\text{H}_2 + \text{OH} = \text{H}_2\text{O} + 64 \text{ Kcal}$ 

| $T^\circ \text{ abs}$ | $K_p =$           | % splitting<br>at 1 atm |
|-----------------------|-------------------|-------------------------|
| 1500                  | $8.87 \cdot 10^5$ | 0.0136                  |
| 2000                  | $3.15 \cdot 10^3$ | 0.586                   |
| 2500                  | 108               | 5.56                    |
| 3000                  | 11                | 26                      |

reaction conditions (page 324). Direct experiments on the concentration of O-atoms in the flame have not yet been made.

<sup>1</sup> KONDRATJEW, V., and M. ZISKIN, *Acta Physicochim. URSS*, **5**, 301 (1936); **6**, 307 (1937); **7**, 65 (1937). AVRAMENKO, L., and V. KONDRATJEW, *Acta Physicochim. URSS*, **7**, 567 (1937).

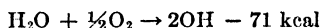
The concentrations of active particles can, by the way, also be considerable in thermal equilibrium, especially the concentrations of H-atoms, and they can sometimes play a role in inducing the reaction and in propagating the explosion in the burning zone of a flame. The concentration of H- and O-atoms can be calculated in advance with certainty from the thermochemical data (of spectroscopic origin). The concentration of OH-radicals has been determined directly by experiment, again by optical means, and first of all by Bonhoeffer and Reichardt.<sup>1</sup>

In Tables 56 to 58 from Zeise,<sup>2</sup> we present a survey of the equilibrium constants of the reactions in question as well as of the degrees of dissociation prevailing at atmospheric pressure.

The degree of splitting of hydrogen in equilibrium (and still more that of oxygen) is therefore so small that, except in the burning zone of a flame, it can hardly play a role. Nevertheless, the few H-atoms present in the equilibrium can sometimes suffice even at low temperatures as starting centers for the chain in a reaction taking place with chain-branching. The degree of splitting of oxygen is still smaller (Table 57).

On the other hand, the splitting of H<sub>2</sub>O into OH and  $\frac{1}{2}$ H<sub>2</sub> can furnish radicals in considerable quantities in the equilibrium even at low temperatures (Table 58).

The splitting of water and the production of OH-radicals is furthered by oxygen, according to the equation



On the kinetics of the reaction in the advanced explosion at high temperatures, nothing specific is as yet known. It might be possible, however, to form indirect conclusions by continuing the theory of flame velocity of Lewis and v. Elbe<sup>3</sup> and by applying it to the values measured in oxygen-hydrogen combustion. It is possible, however, by using the above data on elementary reactions, to give a reaction scheme that certainly produces a rapid reaction in the field of oxygen-hydrogen combustion, as Bonhoeffer<sup>4</sup> has done.

If the following scheme is used as a basis,

- (1)  $\text{H} + \text{O}_2 = \text{OH} + \text{O} - 14 \text{ kcal}$
- (2)  $\text{O} + \text{H}_2 = \text{OH} + \text{H} + 1 \text{ kcal}$
- (3)  $\text{OH} + \text{H}_2 = \text{H}_2\text{O} + \text{H} + 12 \text{ kcal}$

then, after this reaction cycle has run its course, two H-atoms are present for each one originally present. After the cycle has run 100 times, the number of the initial centers has increased  $2^{100} = 10^6$  times, as

<sup>1</sup> BONHOEFFER, K.F., and H. REICHARDT, *Z. physik. Chem.*, Sec. A, **139**, 75 (1928).

<sup>2</sup> ZEISE, H., *Z. Elektrochem.*, **40**, 885 (1934). The equilibrium in question can also be found tabulated in Justi, "Spezifische Wärme, Enthalpie, Entropie, Dissoziation technischer Glase," Julius Springer, Berlin, 1938.

<sup>3</sup> LEWIS, B., and G. v. ELBE, *J. Chem. Phys.*, **2**, 537 (1934).

<sup>4</sup> BONHOEFFER, K.F., *Z. Elektrochem.*, **42**, 449 (1936).

long as the chain-breaking is disregarded. At about 1000° abs, an impact yield of  $\sim 10^{-4}$  is to be expected for reaction (1) with the activation heats estimated above. At atmospheric pressure and an impact number of  $\sim 10^9$ , a time of  $\sim 10^{-5}$  sec would be expected for the course of the cycle, since the reactions (2) and (3) take place so quickly that (1) alone determines the time. To have the cycle run its course 100 times would thus require  $10^{-3}$  sec, a time that is certainly short enough to explain the observed induction times of explosions.

Since the appearance of H and OH in greater concentrations has been demonstrated in oxygen-hydrogen explosions, there should be no findings to contradict the presence of the above mechanism in explosion at higher temperatures, in propagation, and in detonation. For the explanation of explosion limits at lower temperatures, additional reactions must probably be introduced.

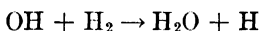
Kondratjew and his associates (cited page 322) conducted oxygen-hydrogen through a quartz tube at temperatures of  $\sim 500^\circ$  to  $600^\circ\text{C}$  at pressures between about 3 and 10 mm Hg and photographed the spectrum. In addition, they determined the amount of water formed (as a measure of the reaction velocity) and, by means of photographs in comparison with the radiation of a Hefner lamp, determined the energy of the radiation emitted (which originates almost exclusively from OH-radicals). The following was found: The entire radiation emitted is by many powers of 10 above that computed for thermal emission; hence we must be dealing with chemiluminescence. Further, the bands show an entirely abnormal intensity distribution. The intensities of the bands ( $0'0''$ ), ( $1'0''$ ), and ( $2'1''$ ) were of the same order of magnitude and were in about the same relation as the transition probabilities.  $0'$ ,  $1'$ , and  $2'$  represent the oscillation quantum numbers  $v'$  for the stimulated, and  $0''$  and  $1''$  correspondingly for the unstimulated OH-radical. The energies for  $v' = 0, 1, 2, 3$  amount to 92.1, 100.5, 108.5, and 116 kcal. In thermal stimulation, a considerable drop in intensity would have to appear in the series of bands emitted from  $0'$ ,  $1'$ ,  $2'$ , . . . , which in reality, however, is not observed before  $v' = 3$ . From this, it is concluded that, as a result of the chemical reaction, an energy  $\geq 108.5$  kcal must be present that suffices for stimulating the conditions till  $v' = 2$  but does not suffice for  $v' = 3$ . Kondratjew would like to make the reaction



responsible for this condition. This energy does not suffice alone, however, and he must therefore assume that the average thermal energies of the three colliding radicals are also available for the stimulus. This robs the theory of some of its convincing force, especially since a Boltzmann factor should be added with the introduction of thermal energy,

and with this factor there would be a decrease of intensity in the bands, which is not observed. We shall therefore suggest a different explanation below. Independent of the explanation, the result is that one light quantum is sent out for about  $10^6$  molecules of water that have formed.

Kondratjew<sup>1</sup> further determined the concentration of OH-radicals in combining oxygen-hydrogen at  $\sim 700^\circ\text{C}$  by means of absorption pictures and found that they are at least forty times greater than corresponds to the equilibrium  $\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} = 2\text{OH}$ . He also determined the concentration of the OH-radicals and the quantity of water formed, and hence the reaction velocity, in mixtures of varied composition and varied pressure. He found both to be proportional to each other (Fig. 170). It is therefore to be assumed that, for water formation, the reactions



in addition to the breaking reaction



are responsible, and this is in agreement with other results.

The formation of water by recombination of H with OH is exothermic with 113 to 115 kcal. If we assume OH as a triple-collision partner in this reaction, it is possible that the reaction energy is used for stimulating the OH bands; and, if we assume the smaller value for the reaction heat to be correct, the observed intensity distribution would be easily understood.

Since Kondratjew finds the OH concentration to be 0.03 per cent at  $\sim 1000^\circ$  abs and  $p_{\text{H}_2+\text{O}_2} = 8$  mm Hg, the fraction of the triple collisions in which OH is the third partner would be  $\sim 3 \cdot 10^{-4}$  of all triple collisions; there are thus about 3000 times as many triple collisions as there are with OH as the third partner. Since a light quantum is emitted only on every  $10^6$ th  $\text{H}_2\text{O}$  molecule that is formed, and since the energy for this is furnished by a triple collision that led to  $\text{H}_2\text{O}$  formation with OH as an impact partner, 3000 times more molecules must have been formed in all in the triple collision; i.e., at least every three hundredth water molecule would have originated from  $\text{H} + \text{OH} + \text{M}$  in the triple collision. This number is not unreasonable and can perhaps yield a point of departure for the breaking probability in triple collision. It is possible that more

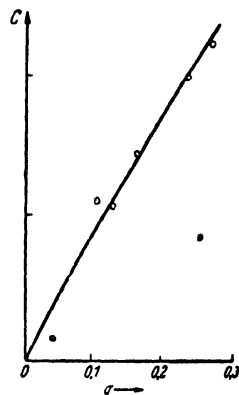


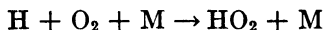
FIG. 170.—Reaction velocity  $q$  and OH concentration  $C$  (arbitrary measure) in oxygen-hydrogen reaction. (From Kondratjew<sup>1</sup>)

<sup>1</sup> KONDRATJEW, V., and L. AVRAMENKO, *Acta Physicochim. URSS*, **7**, 567 (1937).

than every three hundredth  $\text{H}_2\text{O}$  molecule originates in the triple collision, since the energy liberated in every triple collision with OH is not required for stimulating the OH bands.

In an oxygen flame burning in hydrogen, T. Kitagawa<sup>1</sup> observed a complex system of bands between 5500 and 7000 Å, which he interpreted as a rotation oscillation spectrum of the water vapor, since a part of the bands coincided with bands that can be observed in the case of water vapor with a pressure of 2 atm at 144° in layers 8 m thick. The maximum oscillation energy of  $\sim 50$  kcal could come from the reaction  $\text{H} + \text{O}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{OH}$ ; but of course it might just as well have come from the reaction  $\text{H} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O} + \text{M}$ .

*The Theory of Explosion Limits.*—It is hardly necessary to add anything to what has been said about the interpretation of the lower explosion limit (page 294), since the only essential fact is that chain agents are destroyed at the wall. As such, in addition to H, O, and OH,  $\text{HO}_2$ -radicals also come into consideration. For a more detailed discussion, we refer to Lewis and v. Elbe (cited page 300) as well as Kassel and Storch<sup>2</sup> and Kassel.<sup>3</sup> However, the assumption that the reaction

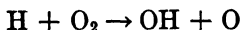


must lead to chain-breaking seems questionable to us; for even at low temperatures a continued reaction of  $\text{HO}_2$  with  $\text{H}_2$  with a reverse formation of H or OH does not seem to be excluded, and at high temperatures this reaction might especially come into play.

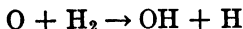
The theory of the upper limit has been discussed by Kassel and especially thoroughly by Lewis and v. Elbe (cited page 300). Like Kassel, they proceed essentially formally by placing at the beginning the relation already established by Semenov that the expression for the reaction velocity

$$w = \frac{n_0}{\beta - \delta}$$

where  $\beta$  is the breaking and  $\delta$  the branching probability, can only then (independent of the concentration of the chain agents) become infinite if  $\beta$  and  $\delta$  are of the same order in respect to the chain agents (page 277). Since, however, we can give only meaningful branching reactions that are of the first order in respect to the active particles, namely,



and



<sup>1</sup> KITAGAWA, T., *Proc. Imp. Acad. Tokyo*, **12**, 281 (1936).

<sup>2</sup> KASSEL, L.S., and H.H. STORCH, *J. Am. Chem. Soc.*, **57**, 672 (1935).

<sup>3</sup> KASSEL, L.S., *Chem. Rev.*, **21**, 331 (1937).

all breaking reactions that are not of the first order in respect to the chain agents are excluded from the start. It has been experimentally demonstrated, however, that triple-collision recombinations taking place according to the second order in respect to active particles, like



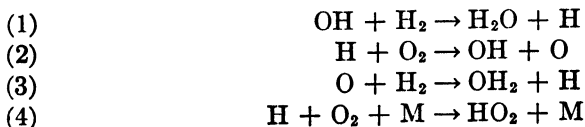
and others, actually occur. It is therefore also experimentally certain that, especially with high concentrations of active particles, the formal expression for the trend toward infinite reaction velocity cannot be fulfilled. This naturally makes no difference at all in the physical fact of the appearance of an explosion, since in reality the reaction velocity likewise does not become infinite and since it is always possible that the reaction velocity proceeds only to the point at which the transition to thermal explosion takes place.

The entire argument, however, suffers also from this defect: The breaking reaction of the second order can be stricken from the reaction scheme only if it can be replaced by another reaction proceeding more rapidly (which generally, however, applies only for the initial stage of the reaction). If, for formal reasons, however, no explosion would result in the breaking reaction of the second order, no explosion could take place at all in a still more rapidly occurring breaking reaction of the first order, and with this the whole theory leads *ad absurdum*. For physical reasons, we should therefore prefer not to follow this line of argument, but we call attention to the fact that the formal statement is correct: An explosion condition in the usual form, according to Semenov, can be derived only for breaking reactions of the first order, although, to be sure, only under the presupposition that the expression for the reaction velocity can be reduced to the form

$$w \sim \frac{n_0}{\tau - \delta}$$

which is by no means self-evident for more complicated reaction results. The author<sup>1</sup> has shown that, in more complicated cases, the condition for a chain explosion can assume an essentially different form (cf. above, page 279).

The reaction scheme that Lewis and v. Elbe give is as follows:



These are all experimentally demonstrated reactions; but it would be necessary to ascribe to  $\text{HO}_2$  a very long life and small reaction possibility

<sup>1</sup> Jost, W., and L. v. MÜFFLING, *Z. physik. Chem., Sec. A*, **183**, 43 (1938).



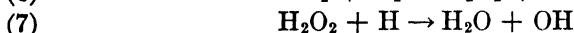
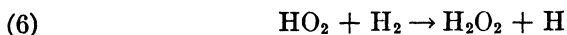
and to assume that it is destroyed at the wall without, however, causing a wall effect and a dependence on the diameter of the container for the upper limit. Then the correct formal relation for the upper explosion limit can be derived.

That the four reactions given above actually take place is, after what has been said, as good as certain. It will not be possible, however, to regard (4) as chain-breaking; it will rather be necessary also to take into account the succeeding reactions that are reasonably to be expected as well as breaking reactions in the gas phase, even though they are not of the first order in the active particles.

We shall perform the computation by including reactions that, after what has been said (pages 316ff.), are at any rate not unreasonable



as a chain-breaking reaction of the second order, as well as



In the usual manner, we compute from this the static reaction velocity and must accordingly first compute, according to Bodenstein, the static concentrations of the intermediary products from the equation system.

$$(I) \quad \frac{d[\text{OH}]}{dt} = k_1[\text{OH}][\text{H}_2] + k_2[\text{H}][\text{O}_2] + k_3[\text{O}][\text{H}_2] + k_7[\text{H}_2\text{O}_2][\text{H}] = 0$$

$$(II) \quad \frac{d[\text{O}]}{dt} = k_2[\text{H}][\text{O}_2] - k_3[\text{O}][\text{H}_2] = 0$$

$$(III) \quad \frac{d[\text{H}]}{dt} = k_1[\text{OH}][\text{H}_2] - k_2[\text{H}][\text{O}_2] + k_3[\text{O}][\text{H}_2] - k_4[\text{H}][\text{O}_2][\text{M}] + k_6[\text{HO}_2][\text{H}_2] - k_7[\text{H}_2\text{O}_2][\text{H}] = 0$$

$$(IV) \quad \frac{d[\text{HO}_2]}{dt} = k_4[\text{H}][\text{O}_2][\text{M}] - 2k_5[\text{HO}_2]^2 - k_6[\text{HO}_2][\text{H}_2] = 0$$

$$(V) \quad \frac{d[\text{H}_2\text{O}_2]}{dt} = k_5[\text{HO}_2]^2 + k_6[\text{HO}_2][\text{H}_2] - k_7[\text{H}_2\text{O}_2][\text{H}] = 0$$

From this, we obtain by means of extensive computation, which can be carried out, however, without disregarding any factors, the concentration of the active particles

$$[\text{OH}] = \frac{k_2 k_6^2 [\text{H}_2] \{k_4 [\text{M}] + k_2\}}{k_1 k_5 \{k_4 [\text{M}] - 2k_2\}^2}$$

$$[\text{H}] = \frac{k_2 k_6^2 [\text{H}_2]^2}{k_5 [\text{O}_2] \{k_4 [\text{M}] - 2k_2\}^2} \quad [\text{H}_2\text{O}_2] = \frac{\{k_4 [\text{M}] - 2k_2\} [\text{O}_2]}{k_7}$$

The expression for  $[H_2O_2]$  loses its meaning if the bracket is  $\{ \dots \} \leq 0$ ; but this is entirely proper, for we shall find this as the explosion condition, and then the above concentrations computed under the presupposition of stationarity will also not be valid.

For the reaction velocity, we obtain with the above values from Eqs. (1) and (7)

$$\frac{d[H_2O]}{dt} = \frac{k_2 k_4 [M] k_6^2 [H_2]^2}{k_6 \{ k_4 [M] - 2k_2 \}^2}$$

This expression no longer has the form of Semenov's expression

$$\frac{n_0}{(\beta - \delta)};$$

nevertheless, it can still become  $\infty$  for

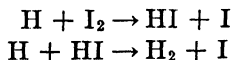
$$k_4 [M] = 2k_2$$

This is identical, however, with the explosion condition found by Hinshelwood and derived theoretically (with doubtful assumptions); for  $[M]$  in the triple-collision reaction (4) means any kind of molecule. If we substitute the individual triple-collision constants  $k_4^{H_2}$ ,  $k_4^{O_2}$ ,  $k_4^A$  for  $H_2$ ,  $O_2$ , and inert gas A as a triple-collision partner, it follows:

$$k_4^{H_2} [H_2] + k_4^{O_2} [O_2] + k_4^A [A] = 2k_2$$

Here the temperature dependence of the upper explosion limit derives chiefly from the temperature dependence of  $k_2$ , even though it might be increased by the fact that the triple-collision yield is reduced with rising temperature. We should not like to assert as yet that the above mechanism must absolutely be the one that actually takes place; at any rate, it suffices to furnish the formal position of the upper explosion limit and requires only reactions the occurrence of which can be regarded as to some extent assured.

The understanding of the reaction inhibition by halogens and halogen-splitting substances, especially iodine, established particularly by Hinshelwood and his associates, offers no difficulties.<sup>1</sup> Reactions like the following might be determining in this case:

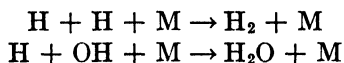


which combine hydrogen atoms and can be regarded as chain-breaking, since the iodine atoms can continue to react only with considerable activation energy and can therefore recombine more readily.

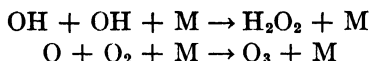
<sup>1</sup> GARSTANG and C.N. HINSHELWOOD, quoted p. 302. HINSHELWOOD and WILLIAMSON, quoted p. 292. Cf. also LEWIS and v. ELBE, "Combustion, Flames and Explosions of Gases."

It is further possible to include the effect of  $\text{NO}_2$  in the general scheme, in which both chain-branching and chain-breaking activity must be attributed to  $\text{NO}_2$ .<sup>1</sup> For details, we refer to the extensive discussion by Lewis and v. Elbe.<sup>2</sup>

*Mechanism of the Reaction above the Upper Explosion Limit.*—It is not difficult to understand that, with increased pressure, the various chain-breaking reactions taking place according to the second order in respect to active particles, such as



or



play an important part and that as a result the reaction mechanism that was a determining factor at the explosion limit becomes much less important. In spite of this fact, the experimental findings are quite remarkable.

For the mechanism of the reaction above the upper limit, see especially Hinshelwood and Williamson (cited page 292) as well as Lewis and v. Elbe.<sup>3</sup> In this range, the reaction is of a high order rising with the pressure and temperature. For the static reaction above the upper limit, it is necessary to introduce the chain-inducing reactions. According to the results of Haber and Alyea (cited page 302), it is not unreasonable to assume with Lewis and v. Elbe that chain induction at the wall takes place below about  $540^\circ$  to  $560^\circ$  but above that in the gas phase. This could account for the fact that, in some experiments, for example, those by Pease (cited page 302), coating the wall with KCl greatly inhibits the reaction; whereas, in other experiments (Hinshelwood and Williamson, cited page 292), such an inhibition is not noted in quartz chambers. It is of course not certain that with Pease chain induction took place at the wall and with Hinshelwood and Williamson it took place in the gas phase. Difficulties for this interpretation arise with the observation that in silver containers<sup>4</sup> the reaction is practically completely suppressed up to about  $700^\circ\text{C}$ . This can be brought into harmony with

<sup>1</sup> In interpreting the effect of antiknock compounds (Chap. XII), similar assumptions will have to be introduced.

<sup>2</sup> Cf. also LEWIS and v. ELBE, "Combustion, Flames and Explosions of Gases." A chain-branching effect is produced by the reaction  $\text{NO}_2 \rightarrow \text{NO} + \text{O}$ , and a chain break in the double collision is conceivable by  $\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2$ .

<sup>3</sup> LEWIS and v. ELBE, "Combustion, Flames and Explosion of Gases;" also *J. Am. Chem. Soc.*, **59**, 656 (1937).

<sup>4</sup> HINSHELWOOD, C.N., E.A. MOELWYN-HUGHES, and A.C. ROLFE, *Proc. Roy. Soc. London, A*, **139**, 521 (1933).

the theory developed only by assuming a chain break in the gas phase, perhaps by silver<sup>1</sup> atomized by the effect of atomic hydrogen. In other assumptions, we should come into conflict with the observations made on the dependence of the reaction velocity on the diameter of the chamber, the condition of the wall, etc. (cf. pages 306ff.).

Lewis and v. Elbe have attempted to make use of these theories quantitatively. We shall omit their computations here; they would have to be drawn upon in any case if this reaction were further developed. The reservations made earlier (pages 320ff.) would naturally have to be taken into account.

For oxygen-hydrogen combustion, cf. also Prettre.<sup>2</sup>

### B. CARBON MONOXIDE COMBUSTION

**1. The Explosion Limits.**—Carbon monoxide combustion shows many similarities to oxygen-hydrogen combustion. The explosion range is entirely analogous to that of oxygen-hydrogen; it is only moved toward higher temperatures by  $\sim 100^\circ$  to  $150^\circ$ .<sup>3</sup> However, the lower explosion limit occurs at somewhat higher pressures than in oxygen-hydrogen explosion. The most striking fact about carbon monoxide oxidation is its great sensitivity to small quantities of water vapor. Completely dry CO-O<sub>2</sub> mixtures react very slowly; small quantities of H<sub>2</sub>O accelerate the reaction considerably. Very well dried CO-O<sub>2</sub> mixtures (i.e., those dried by long contact with P<sub>2</sub>O<sub>5</sub>) do not explode even when one tries to ignite them with an ordinary spark (Dixon<sup>4</sup>). From this, it should not be concluded, however, that the dry mixture does not ignite at all, but only that an essentially higher energy is necessary for ignition than for the ignition of wet mixtures. In reality, later systematic investigations<sup>5</sup> made in the Bone Institute resulted in the following: (2CO + O<sub>2</sub>) mixtures that were charged with water vapor of varying pressures (corresponding to 2.0 to 0.03 per cent by volume) were ignited by condenser discharges. The condenser was always

<sup>1</sup> According to Lewis and v. Elbe, quoted p. 300; cf. BONHOEFFER, K.F., *Z. physik. Chem.*, **113**, 199 (1924).

<sup>2</sup> PRETTRE, M., *L'Inflammation et la combustion explosive en milieu gazeux*, *Act. sci. et ind.*, No. 61, Paris, 1933. Réaction en chaines, *Act. sci. et ind.*, Nos. 425 and 428, Paris, 1936.

<sup>3</sup> SAGULIN, A., *Z. physik. Chem.*, Sec. B, **1**, 275 (1928). KOPP, KOWALSKY, A. SAGULIN, and N. SEMENOFF, *Z. physik. Chem.*, Sec. B, **6**, 307 (1930). SEMENOFF, "Chemical Kinetics and Chain Reactions." HADMAN, G., H.W. THOMPSON, and C.N. HINSHELWOOD, *Proc. Roy. Soc. London*, A, **137**, 87 (1932); **138**, 297 (1932). GARNER, W.E., and A.S. GOMM, *Trans. Faraday Soc.*, **24**, 470 (1928).

<sup>4</sup> DIXON, H.B., *Phil. Trans. Roy. Soc. London*, **175**, 617 (1884). Cf. also Bone and Townsend for further literature.

<sup>5</sup> WESTON, F.R., R.P. FRASER, and D.M. NEWITT, *Proc. Roy. Soc. London*, A, **110**, 615 (1926).

loaded to the same tension of 110 volts, and the capacity was varied so that the minimum capacity required for ignition in the case of each mixture was determined. This was found to be  $0.76 \mu\text{f}$  for the mixture (2 per cent) saturated with water vapor at room temperature, and  $20.83 \mu\text{f}$  for the mixture (with 0.03 per cent  $\text{H}_2\text{O}$ ) dried with  $\text{CaCl}_2$ . The corresponding spark energies are  $4.6 \cdot 10^{-3}$  and  $126 \cdot 10^{-3}$  joule. The corresponding minimum capacities for the range investigated are plotted in Fig. 171. It was also possible to ignite a  $(2\text{CO} + \text{O}_2)$  mixture dried by  $\text{P}_2\text{O}_5$ , but for this a spark energy of 0.362 joule was required; *i.e.*, the discharge of a condenser of  $0.77 \mu\text{f}$  loaded to 970 volts.

The content of water vapor has a powerful effect also on the flame velocity (Chap. III, page 121), the detonation (Chap. V, page 180).

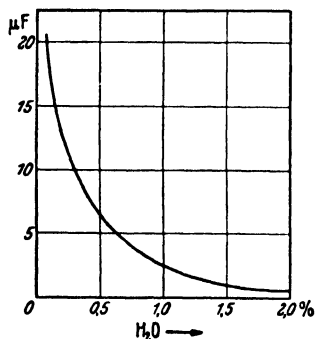


FIG. 171.—Ignition of mixtures of  $2\text{CO} + \text{O}_2$  of varying water vapor content by condenser discharges of 110 V. The minimum capacity required for ignition is plotted. (From Bone, p. 332.)

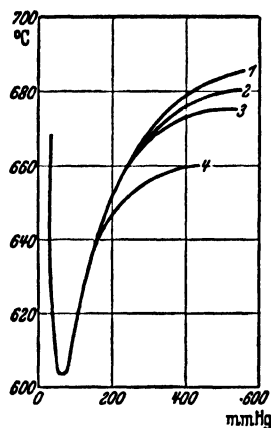


FIG. 172.—Explosion range of  $2\text{CO} + \text{O}_2$ , determined by Sagulin by means of the flow method. Flow velocity 1:1 l in 50 min; 2:1 l in 30 min; 3:1 l in 20 min; 4:1 l in 1 min.

and the radiation of the flames (page 336). Remarkably enough, the position of the explosion limits seems hardly to be influenced by water vapor. Hence, in contrast to the other processes, a mechanism must be suspected here that is independent of added water. At any rate, it must be said that CO combustion has not been investigated with the same thoroughness by far as has oxygen-hydrogen combustion and that a confirmation of many results is desirable.

The position of the explosion limits from the measurements of Semenov's Institute can be seen in Figs. 172 and 173. Figure 172 also reveals the following: The experiments were made according to the flow method; *i.e.*, the mixtures flowed from a storage chamber through the reaction chamber at a definite pressure. The reaction chamber was heated until explosion resulted. By a suitable regulation of the entrance

valve as well as the valve through which the gas was pumped out of the chamber, it was possible to keep the pressure constant at various flow velocities and hence to regulate the duration of the gas in the reaction chamber. Figure 172 gives results with four various flow velocities. Up to the higher pressure range ( $\sim 150$  mm Hg), the explosion limits obtained with various flow velocities coincide with one another; but above that there are systematic variations, and these show that ignition is more difficult the longer the duration of the gas in the reaction chamber, or, in other words, the smaller the flow velocity. Semenoff assumes that reaction products have an inhibiting effect on "high-pressure" explosion. As a result, the flow method is not to be highly recommended for such conditions.

The dependence of the position of the explosion limits on the composition of the mixture can be seen from Fig. 173, likewise taken from Sagulin. The higher the oxygen content of the mixture, the more the explosion limits expand and the lower the ignition temperature, at least in the range investigated. Hinshelwood and his associates (cited page 330) have made similar observations.<sup>1</sup> As proof for the independence of the ignition pressures from the water-vapor content, we present some numerical values from Garner and Gomm,<sup>2</sup> who obtained them in a quartz chamber several centimeters in diameter for mixtures that were moderately dry and also saturated with water vapor at room temperature. For both, the lower explosion limit was situated at a pressure of 0.3 to 0.5 cm Hg (for  $2\text{CO} + \text{O}_2$ ) with the temperature between  $660^\circ$  and  $850^\circ\text{C}$ ; it was practically independent of the temperature. The more exact investigation of Hinshelwood and his collaborators<sup>3</sup> shows that a series of complications can appear. The observations at the lower limit are such as could be expected. Like CO and  $\text{O}_2$ , inert gases have an explosion-stimulating effect. The fact that a clear influence of the chamber dimensions could not be observed might be due to the changing condition of the wall. Coslett and Garner<sup>3</sup> found in addition that, in carrying out a series of provisions for the lower explosion limit in the

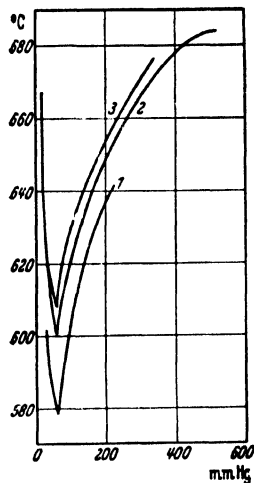


FIG. 173.—Explosion ranges of the mixture  $\text{CO} + 9\text{O}_2$ , 1;  $2\text{CO} + \text{O}_2$ , 2;  $6\text{CO} + \text{O}_2$ , 3. (From Sagulin.)

<sup>1</sup> Cf. also PRETTRE, M., and P. LAFFITTE, *Compt. rend.*, **189**, 177 (1929).

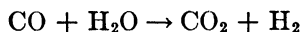
<sup>2</sup> GARNER, W.E., and A.S. GOMM, *Trans. Faraday Soc.*, **24**, 470 (1928).

<sup>3</sup> HADMAN, G., H.W. THOMPSON, and C.N. HINSHELWOOD, *Proc. Roy. Soc. London*, A, **138**, 297 (1932). Cf. also COSLETT, V.E., and W.E. GARNER, *Trans. Faraday Soc.*, **26**, 190 (1930).

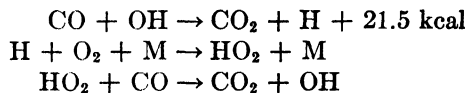
same chamber one after another and then pumping the chamber out each time, the value of the lower limit rose more and more and approached a terminal value. Although ignition was stimulated by argon additions, it was inhibited by  $N_2$  and  $CO_2$  as well as by excess  $CO$ . The upper limit, as could be expected, was found to be independent of the diameter of the chamber. On the other hand, the same value is not found for this limit if the method is varied (if both gases are admitted successively into the chamber, "mixing method," or if the mixture is prepared at high pressure and then pumped off, or, finally, if the mixture is prepared in a cold reaction vessel and then heated). By heating a mixture of dry gases, we enter the explosion range; on the other hand, the pumping off of a mixture prepared above the limit fails. According to Hinshelwood, we are here dealing with peculiar metastability phenomena that seem to be caused by the change in the nature of the wall under the influence of  $CO$ , for by heating the reaction chamber with oxygen they can again be reversed.

Nitric oxide<sup>1</sup> reduces the explosion temperatures, just as it does in the case of oxygen-hydrogen. There is also a sensitizing by means of ammonia.<sup>2</sup>

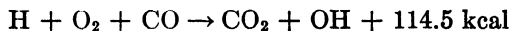
**2. Reaction outside the Explosion Limits.**—In 1905, Bodenstein<sup>3</sup> had already investigated the catalytic oxidation of  $CO$  taking place at low temperatures. The catalytic combustion of  $CO$  on quartz surfaces is inhibited by water,<sup>4</sup> whereas the gas reaction is greatly accelerated by water vapor. The role that water vapor plays in  $CO$  combustion has been known for a long time and was formulated by Dixon in the following manner:



with combustion of the hydrogen following immediately. Even though this reaction is not excluded, it seems more probably that a chain reaction takes place with the same chain agents as in  $H_2$  combustion, and the appearance of  $OH$  bands in the combustion of wet  $CO$  favors this view. For this, the following reactions among others would come into consideration:



or also the triple-collision reaction



<sup>1</sup> SAGULIN, quoted p. 331.

<sup>2</sup> FARKAS, F. HABER, and P. HARTECK, *Naturwissenschaften*, **18**, 266 (1930).

<sup>3</sup> BODENSTEIN, M., and OHLMER, *Z. physik. Chem.*, **53**, 166 (1905).

<sup>4</sup> BRADFORD, B.W., *J. Chem. Soc.*, 1933, p. 73.

If the chain reactions of oxygen-hydrogen combustion play a role, especially with H-atoms taking part, we should observe inhibitions

TABLE 59.—REACTION VELOCITY OF 50 MM CO + 250 MM O<sub>2</sub> AT 560°C IN THE PRESENCE OF WATER VAPOR

| $p_{H_2O}$ ,<br>mm Hg | Initial reaction velocity, mm decrease<br>in pressure/min |
|-----------------------|---|
| 10                    | 2.1   |
| 15                    | 3.2   |
| 20                    | 3.9   |
| 25                    | 5.2   |

TABLE 60.—REACTION VELOCITY OF 100 MM CO + 15 MM H<sub>2</sub>O + 0.4 MM I<sub>2</sub>

| With mm O <sub>2</sub> | Reaction velocity |
|------------------------|-------------------|
| 50                     | 1.0               |
| 100                    | 1.3               |
| 200                    | 1.8               |

of the reaction by additions similar to those in oxygen-hydrogen combustion. Hadman, Thompson, and Hinshelwood<sup>1</sup> actually found such an inhibition. The highest temperature at which, without the addition of iodine, the reaction velocity could conveniently be measured under the experimental conditions of Hinshelwood and Thompson was 580°C. With small additions of iodine, on the other hand, the reaction velocity was too small for exact measurement and still measurable at 100° above the former temperature. At constant temperature, the ratio of the reaction velocity with and without iodine of 1 mm pressure is about 100:1. Further, the usual influence of the chamber dimensions on the reaction velocity disappears in the presence of iodine, a sign that the reaction chains normally broken off by iodine at the wall are now broken off in the gas phase. For example, the reaction velocity in the presence of iodine in the largest and in the smallest reaction chamber at 680° is in the ratio of about 3:1, whereas this ratio without iodine at 600° is 300:1.

With this, it is also possible to gain an understanding of the inhibition by oxygen present in slow reactions. If this extended to the primary process, it would have to be present also in the presence of iodine; but, if it consists in a stimulation of chain-breaking (at the wall), it should disappear when most of the chains in the gas phase are broken by iodine. Actually, the oxygen inhibition disappears with the addition of iodine. Several quantitative figures can be obtained from Tables 59 and 60.

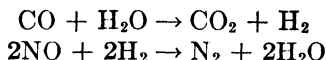
The reaction velocity is therefore proportional to the H<sub>2</sub>O concentration. In the wet mixture, the reaction velocity is directly proportional

<sup>1</sup> HADMAN, G., H.W. THOMPSON, and C.N. HINSHELWOOD, *Proc. Roy. Soc. London*, A, **137**, 87 (1932).

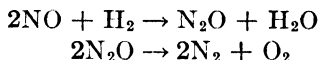


to the CO concentration, and inversely proportional to the O<sub>2</sub> concentration. Table 60 gives information on the disappearance of the O inhibition in the presence of iodine.

The oxidation of CO with NO in the presence of water vapor obeys relatively simple laws.<sup>1</sup> It appears to be formally possible to explain the observed velocity by the equation



if the latter process is thought of in two steps



of which the first is velocity-inhibiting. That the reaction takes place through hydrogen is not rendered improbable by observing an inhibiting effect of Br<sub>2</sub>, which utilizes hydrogen. This would rather suggest that H-atoms are participating.

**3. Spectroscopic Investigations of CO Combustion. CO Explosions in the Presence of Nitrogen.**—Spectroscopic investigation has also contributed to the explanation of the mechanism in CO combustion. In the explosion of CO-O<sub>2</sub> mixtures, an intensive violet-red luminescence is observed during the induction period of several seconds, also at temperatures of ~ 50° to 60° below the flaming temperature.<sup>2</sup> The radiation of the CO flame comes chiefly from the CO<sub>2</sub>-molecule.<sup>3</sup> In the infrared, one can observe maxima at 2.8 and 4.5 μ; here a part of the radiation is absorbed by CO in the infrared,<sup>4</sup> for which reason minima corresponding to the CO bands are obtained at 2.3 and 4.7 μ. An influence of this radiation, absorbed by CO, on the reaction velocity does not exist, as has been definitely shown by Garner and Gomm by special experiments with CO-O<sub>2</sub> mixtures that reacted in quartz chambers at 750° just under the critical explosion pressure with and without infrared radiation.

Nitrogen plays a remarkable role in carbon monoxide combustion.<sup>5</sup> In 1909, Haber and Coates published experiments on NO formation in a CO-air flame burning under pressure.<sup>6</sup> They proceeded on the assumption that ions appear in the flames and that perhaps under the influence of these gas ions more NO might be produced than would correspond to

<sup>1</sup> MUSGRAVE, F.F., and C.N. HINSHELWOOD, *J. Chem. Soc.*, 1933, p. 56.

<sup>2</sup> PRETTRE, M., and P. LAFFITTE, *Compt. rend.*, **189**, 177 (1929).

<sup>3</sup> KONDRATJEW, V., *Z. Physik*, **63**, 322 (1930).

<sup>4</sup> GARNER, W.E., and A.S. GOMM, *Trans. Faraday Soc.*, **24**, 470 (1928).

<sup>5</sup> In this connection, see BONE and TOWNEND, "Flame and Combustion in Cases," as well as BONE, NEWITT, and TOWNEND, "Gaseous Combustion at High Pressures."

<sup>6</sup> HABER, F., and COATES, *Z. physik. Chem.*, **69**, 337 (1909).

the thermal equilibrium between  $N_2 + O_2$ . It might be well to point out that no contradiction to thermodynamics is implied. If an  $N_2 + O_2$  mixture is heated to a certain temperature by a  $CO-O_2$  explosion and NO is then permitted to form, the formation cannot of course exceed the equilibrium concentration. The case is different, however, if from the beginning the  $CO + O_2$  and the  $N_2 + O_2$  reactions are coupled with one another, for then the NO concentration reached can very well be higher than corresponds to the equilibrium of the components in the terminal condition. This no more contradicts thermodynamics than does the fact that more H-atoms are produced in oxygen-hydrogen explosions with chain-branching than corresponds to the dissociation equilibrium of  $H_2$ . In both cases, the condition is that conversion in the total system has taken place with a decrease of free energy in reference to the initial condition. Further, the concentration of a component like that of NO in excess of equilibrium present in the terminal condition can maintain itself only for a short time, because the system naturally strives for equilibrium unless the reaction velocity is decreased exceedingly by cooling.

Haber and Coates could not prove the presence of NO quantities beyond equilibrium with any certainty. However, Bone and his associates<sup>1</sup> found yields in excess of equilibrium that were further increased by suddenly cooling the gases immediately upon reaching the maximum temperature. (This was done as follows: The explosion bomb was divided by means of a suitable membrane that was so proportioned and constructed that the mixture filling one side of the bomb was exploded, the membrane was then pierced after a short interval, and the gas was thus suddenly expanded to a greater volume.) The addition of nitrogen to  $CO-O_2$  mixtures decreases the flame velocity considerably and cor-

TABLE 61.—NO FORMATION IN CO EXPLOSIONS (FROM BONE)

| Mixture                       | Initial pressure, atm | Terminal pressure, atm | Maximum temperature, $T^\circ$ abs | NO formation, % in cold products <sup>1</sup> |
|-------------------------------|-----------------------|------------------------|------------------------------------|---|
| $2CO + 1.25O_2 + 5N_2$ .....  | 125                   | 960                    | 2270                               | 2.4   |
| $2CO + 1.5O_2 + 6N_2$ .....   | 125                   | 750                    | 1740                               | 2.2   |
| $2CO + 1.6O_2 + 6.4N_2$ ..... | 125                   | 720                    | 1660                               | 2.0   |

<sup>1</sup> The concentration, corresponding to  $O_2$  and  $N_2$  still present, is correspondingly higher; similarly in the following experiments.

<sup>1</sup> Cf. especially BONE, NEWITT, and TOWNEND, "Gaseous Combustion at High Pressures"; also BONE, W.A., D.M. NEWITT, and D.T.A. TOWNEND, *Proc. Roy. Soc. London*, A, **139**, 57 (1933). TOWNEND and L.E. OUTRIDGE, *Proc. Roy. Soc. London*, A, **139**, 74 (1933). NEWITT, D.M., and F.G. LAMONT, *Proc. Roy. Soc. London*, A, **139**, 83 (1933).

respondingly increases sharply the time elapsing until the maximum pressure is reached.

We shall now give several experiments by Bone and his associates: According to Zeise (cited page 323), the equilibrium concentration in a ( $1\text{N}_2 + 1\text{O}_2$ ) mixture amounts to 0.205 per cent at 1600 abs, and to 1.38 per cent at 2200°; for the mixture above, it is correspondingly less. Since the preceding experiments are carried out without cooling, and hence a part of the NO has certainly been lost, NO concentrations above equilibrium will doubtless be found.<sup>1</sup>

In experiments with a broken pane, an increased NO production took place. In an initial mixture of  $2\text{CO} + 3\text{O}_2 + 2\text{N}_2$  at  $P_{\text{initial}} = 72$  atm,  $P$  (at breaking of pane) = 630 atm,  $T_{\text{max}} = 2815^\circ$  abs, and 5.4 per cent  $\text{NO}_2$  were found in the cold terminal gases.<sup>2</sup>

By means of experiments in which the pane is broken at various time intervals before and after reaching the maximum pressure, it was shown (cf. Table 62) that NO formation begins during combustion but still continues during the cooling (which at first is delayed).

In static high-pressure flames, the maximum yield of NO is about 2 per cent. That NO formation is no purely thermal phenomenon is clear from further experiments by Bone in which he compared explosions

TABLE 62.—EXAMPLE:  $P_a$  ABOUT 70 ATM (INITIAL MIXTURE  $2\text{CO} + 3\text{O}_2 + 2\text{N}_2$ )

| $P_a$ , atm | $P$ (at the breaking of the glass), atm | Moment of breaking; before or after reaching $P_{\text{max}}$ | $T_{\text{max}}$ ° abs | % $\text{NO}_2^1$ | % NO computed |
|-------------|---|---|------------------------|-------------------|---------------|
| 70          | 520                                     | −0.03   | —                      | 3.3               | —             |
| 68          | 635                                     | +0.02   | 2915                   | 4.5               | 2.3           |
| 70          | 620                                     | +0.06   | 2815                   | 5.4               | 2             |
| 72          | 630                                     | +0.13   | 2815                   | 5.4               | 2             |

<sup>1</sup> Originally, of course, NO is formed, but in cooling it combines with excess oxygen to form  $\text{NO}_2$ .

of  $2\text{CO} + 3\text{O}_2 + 2\text{N}_2$  with those of  $2\text{H}_2 + 3\text{O}_2 + 2\text{N}_2$ . Up to 3 per cent NO survived in the CO explosion, but only 0.07 per cent could be established in the  $\text{H}_2$  explosion.<sup>3</sup> Bone has also investigated the processes spectroscopically and concludes that an activation of the  $\text{N}_2$ -molecule (by means of transmission through impacts of the second kind) must be the primary process. In an explosion of  $2\text{CO} + 1.25\text{O}_2 + 5\text{N}_2$  and 25 atm of initial pressure, for example, a bright orange-yellow flame

<sup>1</sup> A process for obtaining NO by means of gas explosion has, by the way, been patented by F. Häusser, DRP 232,569.

<sup>2</sup> Originally, of course, NO is formed, but upon cooling this converts to  $\text{NO}_2$  with the excess of oxygen.

<sup>3</sup> Possibly the question should also be discussed as to whether the NO-destroying reactions take an especially rapid course in  $\text{H}_2$  explosions.

was visually observed, followed by a red after-glow that lasted some time. In the cooled gases,  $\text{NO}_2$  can be shown to be present in absorption. The decreased cooling velocity after reaching the maximum pressure is also striking in explosions in the presence of  $\text{N}_2$ . This fact points to the course of an exothermic conversion.

The role of water vapor in combustion is likewise clarified by spectroscopic observations. As has already been mentioned, "wet" CO explosions as well as  $\text{H}$  explosions yield an intensive spectrum of the OH bands. Although these bands are intensified in  $\text{H}_2$  explosions by raising the initial pressure, they conversely decrease with increasing pressure in CO explosions and disappear at about 30 atm of initial pressure (Bone and Lamont<sup>1</sup>). This observation at least does not contradict the conclusion that the combustion mechanism in wet  $\text{CO-O}_2$  mixtures changes with increased pressure and probably changes over into that of "dry" CO combustion. Naturally, an extinguishing of the luminescent radiation also takes place with increased pressure; hence the conclusion is not entirely convincing. Since the OH bands survive in  $\text{H}_2$  explosions, however, this is not necessarily the reason for their disappearance in CO.

The conditions in CO combustion—without and with water vapor, without and with nitrogen—became much clearer on the basis of quantitative spectroscopic experiments of Kondratjew. That the activation of the nitrogen in Bone's experiments and the lessening of the radiation demonstrated by him in the blue and ultraviolet when nitrogen was added cannot be due to an absorption by nitrogen is clear from its position in the extreme Schumann range. Rather, it can only be a matter of energy transference in impacts of the second kind. Kondratjew<sup>2</sup> has shown directly that, in the combustion of  $\text{CO} + \text{O}_2$ , for example, the mercury resonance line is stimulated at 2537 Å. Since the short-wave end of the spectrum of CO combustion is situated at  $\sim 2200$  Å, a corresponding activation energy up to  $\sim 5.65$  volts can be furnished. The lowest stimulus condition of nitrogen is the metastable  $^3\Sigma$  combustion with a stimulus energy  $^3\Sigma - ^1\Sigma$  of  $6.1 \pm 0.5$  volts, so that either the energy of the  $\text{CO}_2^*$ -molecules,<sup>3</sup> which are probably responsible for the radiation of the CO flames, suffices for stimulating this condition, or at least a remaining difference of the thermal energy can be supplied.

Kondratjew<sup>4</sup> has also succeeded in measuring the total radiation of a  $\text{CO-O}_2$  flame in the visible and in the ultraviolet under conditions

<sup>1</sup> BONE, W.A., and F.G. LAMONT, *Proc. Roy. Soc. London, A*, **144**, 250 (1934).

<sup>2</sup> KONDRATJEW, V., *Acta physicochim. URSS*, **2**, 126 (1935). Cf. also KONDRATJEW, V., *Acta Phys. Polon.*, **5**, 65 (1936).

<sup>3</sup> KONDRATJEW, V., *Z. Physik.*, **63**, 322 (1930).

<sup>4</sup> KONDRATJEW, H., and V. KONDRATJEW, *Acta Physicochim. URSS*, **6**, 748 (1937).

that enabled him to follow the reaction velocity at the same time. He found that, for  $\sim 125$   $\text{CO}_2$ -molecules formed, one  $\text{CO}_2^*$ -molecule must have been formed with the stimulus energy for radiation. In the quantita-

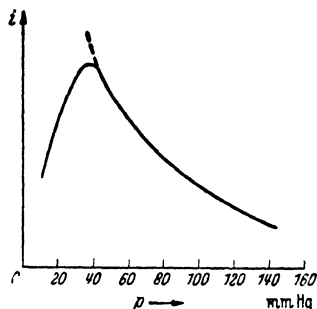
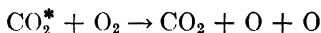


FIG. 174.—Yield of light  $i$  in the reaction of  $2\text{CO} + \text{O}_2$  at  $\sim 740^\circ\text{C}$  as a function of the pressure. (From Kondratjew.)

tative analysis, the extinguishing of the chemiluminescence radiation had to be taken into account. The experiments refer to a quartz container with a volume of  $69 \text{ cm}^3$  through which mixtures of  $\text{CO} + \text{O}_2$ , or  $2\text{CO} + \text{O}_2$  were conducted at  $740^\circ\text{C}$  and about 100 mm pressure with a flow rate of 1 to  $1.5 \text{ cm}^3/\text{sec}$ ; the conversions were between 2.3 and 7.7 per cent, and the radiation intensity was proportional to the conversion. The concentration computed from the emitted radiation of stimulated  $\text{CO}_2^*$ -molecules is greater by  $\sim 10^{18}$  than corresponds to the temperature equilibrium. Accordingly, it seems not unlikely that the chain-branching reaction



plays a role in the combustion.

In earlier works, Kondratjew and Kondratjewa had investigated the radiation of  $\text{CO} + \text{O}_2$  flames in dependence on the pressure and the composition of the gas.<sup>1</sup> The following resulted: At low pressures, the light yield rose initially with the pressure and then dropped above 40 mm approximately according to a hyperbolic law (Fig. 174).

For the hyperbolic portion, the following is valid, if  $p$  is measured in mm Hg:

$$i = \frac{i}{1 + kp} \quad (9)$$

with  $k = 0.113 \text{ mm}^{-1}$ , a law that is commonly found for the extinguishing of luminescence or fluorescent radiation.<sup>2</sup> The numerical value corresponds approximately to an extinguishing at every gas-kinetic impact. This means that the molecule emitting the radiation, say  $\text{CO}_2^*$ , which still bears a great reaction energy, can, during its life of  $\sim 10^{-8} \text{ sec}$ , experience a collision and thus give up its energy before it is able to radiate it. For this, we obtain theoretically the hyperbolic curve and Eq. (9). That the radiation intensity does not rise further at lower pressures but even drops has a trivial reason: At lower pressures, the

<sup>1</sup> KONDRATJEW, H., and V. KONDRATJEW, *Acta Physicochim. URSS*, **4** 547 (1936); **6**, 625 (1937).

<sup>2</sup> Cf. STERN, O., and M. VOLMER, *Physik. Z.*, **20**, 183 (1919).

reaction velocity might drop sharply, and conversion sometimes take place essentially at the wall under conditions in which little or no radiation is emitted. The experiments again refer to a temperature of  $740^{\circ}\text{C}$ . According to Johnson,<sup>1</sup> 10 per cent of the entire energy of  $\text{CO} + \text{O}_2$  at 472 mm pressure is given off in the reaction in the form of infrared, visible, and ultraviolet radiation. Experiments with varying composition [(1)  $p_{\text{CO}} = 40$  mm,  $p_{\text{O}_2} = 20$  to 360 mm; (2)  $p_{\text{O}_2} = 20$  mm,  $p_{\text{CO}} = 40$  to 80 mm; (3)  $p_{\text{total}} = 57$  mm, per cent  $\text{CO} = 20$  to 80; (4)  $p_{\text{CO}} = 40$  mm,  $p_{\text{O}_2} = 20$  mm,  $p_{\text{N}_2} = 0$  to 440 mm] as well as with added nitrogen resulted in the following: For the extinguishing constants, we find, respectively,  $k_{\text{O}_2} = 0.162 \text{ mm}^{-1}$  and  $k_{\text{CO}} = 0.034 \text{ mm}^{-1}$ ; *i.e.*, oxygen quenches luminescence about five times more effectively than carbon monoxide. Conversion was also determined, and at  $740^{\circ}$  it was found that  $\text{CO}$  inhibits

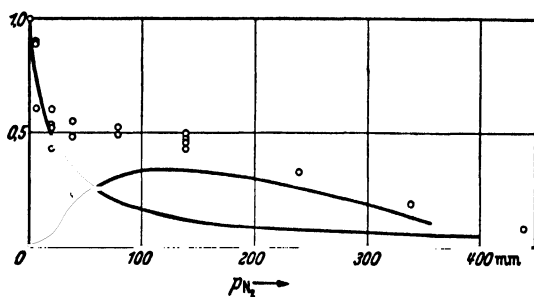


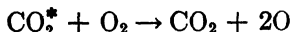
FIG. 175.—Relative yield of light in the reaction of  $2\text{CO} + \text{O}_2$  in the presence of nitrogen with varying pressure. (From Kondratjew.)

it and  $\text{O}_2$  stimulates it. The observations with respect to nitrogen are again singular, but they can be brought into agreement with what Bone's experiments show. Figure 175 gives the experimental results indicating the relative light intensity varying with the  $\text{N}_2$  pressure. Here there is no regular decrease with increased pressure. The observations are to be interpreted formally by the overlapping of two curves, a hyperbolic extinguishing curve with  $k_{\text{N}_2} = 0.28 \text{ mm}^{-1}$ . This especially high extinguishing constant for nitrogen should be brought into relation with the nitrogen activation observed by Bone. The second curve, which shows an increase of intensity with increasing pressure, has its maximum in the same region as the curve of percentage conversion, which is also at first stimulated by nitrogen. It is therefore likely that, in the presence of  $\text{N}_2$ , a supplementary reaction takes place, probably induced by  $\text{NO}$  that is formed, and that this reaction is responsible for the increased radiation.

That oxygen quenches luminescence so much more effectively than

<sup>1</sup> JOHNSON, C.H., *Phil. Mag.*, **5**, 301 (1928).

CO might be due to the fact that the following process is possible with oxygen:



which would again point to the role of this process as a chain-branching reaction.

In the presence of water vapor, the radiation of the carbon monoxide flame decreases.<sup>1</sup> Kondratjew and Kondratjewa<sup>2</sup> have made detailed investigations of these conditions by having  $[\text{CO} + \text{O}_2(+\text{H}_2\text{O})]$  mixtures at about 60 mm pressure and 740°C flow through a quartz chamber and then determining the yield. If the light intensity  $i$  is plotted at water-vapor pressure  $p_{\text{H}_2\text{O}}$  as a function of this pressure, a curve is obtained that is represented by

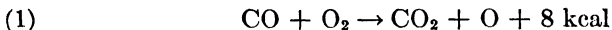
$$\frac{i}{i_0} = \frac{1}{1 + 2.5p_{\text{H}_2\text{O}}}$$

In this,  $i_0$  is the light intensity in the absence of water vapor, but small quantities of  $\text{H}_2$  (from the electrolytic production of oxygen) are still present. This relation must not, however, be interpreted as such for the quenching of a fluorescence, since we should obtain meaninglessly high effectiveness cross sections. It is thus necessary to assume that, in the presence of  $\text{H}_2\text{O}$ , the reaction proceeds partly according to another mechanism and that therefore the light yield is reduced.

If we freed the mixture of the small quantities of  $\text{H}_2$  it contains, the light intensity would drop below the value of  $i_0$  in the absence of  $\text{H}_2\text{O}$ . This is due to the greatly decreased conversion. Conversion rises from a few per cent in dry mixtures to  $\sim 100$  per cent at 0.5 mm  $\text{H}_2\text{O}$ .

Even though a quantitative evaluation of the experiments appears uncertain up to the present, the results agree very well with the other observations.

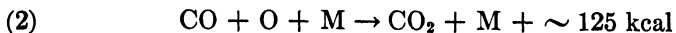
**4. The Mechanism of CO Combustion.**—Somewhat less is known about the mechanism of combustion of CO than about that of  $\text{H}_2$  combustion. It is difficult to formulate a chain reaction without the participation of energy chains. The reaction



<sup>1</sup> GARNER, W.E., and associates, C.H. JOHNSON, *Phil. Mag.*, **5**, 301 (1928). GARNER and JOHNSON, *J. Chem. Soc.*, 1928, p. 218. GARNER and F. ROFFEY, *J. Chem. Soc.*, 1929, p. 1123. GARNER and D.A. HALL, *J. Chem. Soc.*, 1936, p. 2037. GARNER, HALL, and F.E. HARVEY, *J. Chem. Soc.*, 1931, p. 641. BAWN, C.E.H., and GARNER, *J. Chem. Soc.*, 1932, p. 129. GARNER and F.H. POLLAND, *J. Chem. Soc.*, 1935, p. 144. Also WESTON, F.R., *Proc. Roy. Soc. London, A*, **109**, 176, 523 (1925).

<sup>2</sup> KONDRATJEWA, H., and V. KONDRATJEW, *Acta Physicochim. URSS*, **8**, 487 (1938).

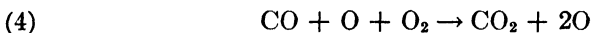
is in itself exothermic. It would therefore be conceivable that it proceeds with an activation heat that would not exclude a participation as a chain-inducing reaction at higher temperatures. The oxygen atoms, however, are not suited for continuing a chain, for with the reaction



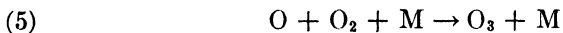
the chain would already be broken. This reaction takes place at about every fortieth triple collision, as can be concluded from photochemical experiments by Groth<sup>1</sup> in the Schumann range. At this place, however, stimulated  $\text{CO}_2^*$ -molecules can originate with an energy that suffices for the dissociation of the oxygen, and the reaction can therefore follow



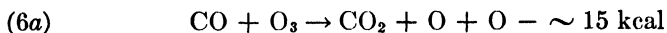
insofar as oxygen has not been effective as a triple-collision partner and the dissociation has taken place in one step



According to Kondratjew, evidence for this reaction exists. Since, according to Kondratjew, one  $\text{CO}_2^*$ -molecule capable of radiation emission arises for every one hundred twenty-fifth  $\text{CO}_2$ , it would be conceivable that reactions (2) and (4) take place oftener than once in 125, since the stimulus energy needs to remain with the  $\text{CO}_2^*$  only in the most favorable cases, whereas it will otherwise distribute itself over the collision partners. By means of the reactions (2), (3), and (4), the stimulation of the reaction by  $\text{O}_2$  and the inhibition by CO could also be understood, since the continuation of the chain, which is in this case identical with branching, can take place only with  $\text{O}_2$  as a triple-collision partner. Reaction (2) would be chain-breaking if no  $\text{CO}_2^*$  were formed or if the latter were formed at first, but a further impact of  $\text{CO}_2^*$  does not lead to oxygen splitting. Since O-atoms with  $\text{O}_2$  furnish  $\text{O}_3$  in abundant yield in the triple collision, a participation of ozone in the reaction is not excluded. It might occur according to



and sometimes, with chain-branching,

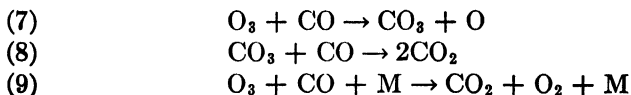


The attempt at a quantitative interpretation of the explosion limits seems premature to us as long as no direct experimental material on the elementary reactions exists. That determining the upper limit must be done

<sup>1</sup> GROTH, W., *Z. physik. Chem.*, Sec. B, **37**, 315 (1937). Cf. also GROTH, W., and P. HARTECK, *Z. Elektrochem.*, **44**, 621 (1938), footnote 1, p. 627.

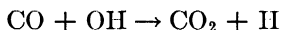


by introducing suitable gas-phase deactivation is certain considering everything hitherto known. Lewis and v. Elbe<sup>1</sup> arrive at a formal interpretation of the upper explosion limit by introducing also the reactions with ozone:

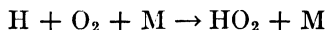


But the introduction of  $\text{CO}_3 \left( \text{O} \begin{array}{c} \diagup \text{O} \\ \diagdown \text{O} \end{array} \right)$  for this purpose, for which there is no experimental evidence, seems for the time being very unsatisfactory. In addition it would appear to us that reaction (7) is highly improbable, even if its existence were admitted. Much more reasonable would be reaction (6). Lewis and v. Elbe have computed this mechanism in order to show that the experiments can be formally accounted for without introducing energy chains, which are in most cases quite improbable. But in this case it happens that there is a direct experimental foundation for energy chains on the basis of Kondratjew's experiments, while, conversely, such an experimental foundation is lacking for the Lewis-v. Elbe material chain.

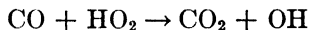
The combustion of wet CO (or of CO in the presence of  $\text{H}_2$  or  $\text{H}_2$ -containing materials) probably proceeds similar to  $\text{H}_2$ -combustion. The reaction



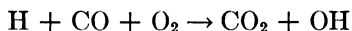
does not appear unlikely. Several come into consideration as succeeding reactions, like



followed by



Equivalent to this would be the triple-collision reaction<sup>2</sup>



which still takes place at the temperature of liquid air and therefore probably with a very small activation heat. Also the reaction



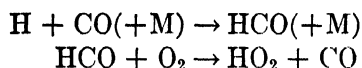
occurs, followed by a  $2\text{HCO} \rightarrow \text{H}_2\text{C}_2\text{O}_2$  (glyoxol) or  $\text{HCO} + \text{H} \rightarrow \text{H}_2\text{CO}$ , or  $\text{HCO} + \text{H}_2 \rightarrow \text{H}_2\text{CO} + \text{H}$  (formaldehyde), as is clear from the

<sup>1</sup> LEWIS, B., and G. v. ELBE, *J. Amer. Chem. Soc.*, **59**, 2025 (1937). Also "Combustion," 1938.

<sup>2</sup> Cf. GEIB, cited, p. 31.

Hg-sensitized photoreaction according to Frankenburg.<sup>1</sup> On the other hand, (10) is successful in only a small fraction of the triple collisions (cf. Geib, cited page 315).

According to Harteck and Groth,<sup>2</sup> the following reaction also takes place:



which need not be especially considered here, however, since it leaves the CO unchanged in the end result.

<sup>1</sup> FRANKENBURGER, W., *Z. Elektrochem.*, **36**, 757 (1930). GROTH, W., cited p. 343.

<sup>2</sup> HARTECK, P., W. GROTH, and K. FALTINGS, *Z. Elektrochem.*, **44**, 621 (1938).

## CHAPTER X

### SPARK IGNITION II: REACTION IN ELECTRICAL DISCHARGES

In Chap. II, we presented some preliminary remarks on spark ignition from the standpoint of theory of heat, which is inadequate for this purpose and accounts for only a part of the phenomena. For a treatment of the question of when and how an explosion induced in a partial volume spreads, it is of small importance by what means this partial explosion was originally caused. For that reason, the necessarily one-sided treatment by way of the theory of heat nevertheless leads to important insights, although, of course, they need supplementation. How the question of spark ignition was regarded even a short time ago is shown by a remark in Bone's book<sup>1</sup> that essential differences of opinion existed as to whether the ignition properties of a spark should be ascribed chiefly to its temperature or to its ionizing effect. According to more recent experiences, it is possible to conclude that the ignition properties of a spark may be ascribed to its ionizing effect almost not at all; to its thermal effect only partly; but to the molecular stimulation and eventual dissociation in the spark to a considerable extent.

**1. Nature of the Spark Discharge. Older Investigations on the Ignition Properties of Various Sparks.**—In older investigations, *e.g.*, by Thornton,<sup>2</sup> the minimum current intensities were determined that were necessary for ignition under predetermined conditions. This was accomplished, for example, by producing an opening spark in a circuit in which a known current was flowing.

For unequivocal results, it is necessary to produce discharges under defined conditions, in other words, either condenser discharges or inductor discharges, if the spark characteristics of the inductor are accurately known. The discharge of a condenser, in the absence of larger self-inductions, takes place in a very short time, *e.g.*,  $\sim 10^{-6}$  sec, from which it follows that the current intensity during the discharge must assume exceedingly high values. The discharge also oscillates with a very high frequency, as can be seen from the fact that the entire discharge period is so short. The discharge of an inductor consists in its very first part, which is known in the English literature as "capacity component," of a corresponding discharge of short duration and of very high frequency

<sup>1</sup> "Flame and Combustion in Gases."

<sup>2</sup> THORNTON, W.M., *Proc. Roy. Soc. London*, A, **90**, 277 (1914); **91**, 17 (1914); **92**, 9, 381 (1915).

and intensity for which the auto-capacity of the secondary coil of the inductor is responsible. Upon the capacity components of a very short duration, there then follows the so-called "inductance component" of essentially longer duration (several thousandths of a second) and essentially smaller intensity. The current decreases exponentially in this period, in which sine oscillations are superimposed on it, whose frequency is essentially expressed by the characteristic frequency of the primary circuit of the inductor, consisting of self-induction and capacity (not exact because of the coupling of the primary and secondary circuit).<sup>1</sup> Theoretically and experimentally, the conditions for spark discharge have been investigated particularly carefully by Finch and his associates.<sup>2</sup>

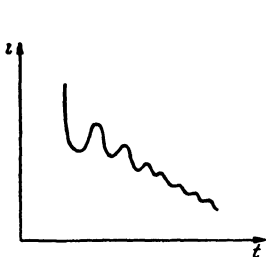


FIG. 176.

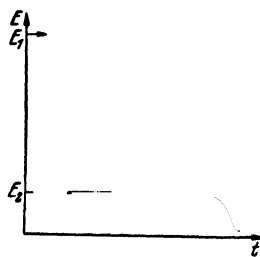


FIG. 177.

FIGS. 176 and 177.—Variations in the current and voltage during the inductance components of an inductor discharge, qualitative. (From Finch.)

In a special apparatus, the frequency of the capacity components was  $\sim 10^7$ , the maximum intensity was  $\sim 113$  amp, the frequency of the inductance components was  $\sim 10,000$ , the current intensity was of the order of magnitude 0.3 amp, the amplitudes of the oscillations were of the order of magnitude 0.1 amp, and the total duration was  $\sim 1.23$  m sec. Qualitatively the following picture resulted for current and voltage as a function of the time [the capacity component is not shown, since it takes place too rapidly and the amplitude is too large (Figs. 176, 177, and 183)]. The voltage first rises to the value of the erupting field strength  $E_1$  and then drops to the value  $E_2$ , where it remains practically constant. The current fades away exponentially with superimposed oscillations but always maintains the same direction. What is shown qualitatively in these figures can be directly determined quantitatively by means of cathode-ray oscillograms (Finch and Sutton, Bradford and

<sup>1</sup> Cf. in this connection "Handbuch der Physik," Vol. 16, pp. 88ff. MÜLLER-POUILLET, "Lehrbuch der Physik," Vol. IV/1, pp. 579ff. and especially E. TAYLOR-JONES, "Induction Coil Theory and Applications," Pitman, London, 1932.

<sup>2</sup> FINCH, G.I., and R.W. SUTTON, *Proc. Phys. Soc. London*, **45**, 288 (1933). See also the critical report, written from the modern point of view, on ignition by electrical discharges by B.W. Bradford and G.I. Finch, [*Chem. Rev.*, **21**, 221 (1937), with extensive bibliography], which we shall follow extensively in the following pages.

Finch, page 347). This can be seen in the spark itself<sup>1</sup> by observing it in a rotating mirror (cf. Taylor-Jones,<sup>2</sup> Fig. 61, page 122). Further (weaker) discharges periodically follow the first spark of the capacity components.

Very early experiments were attempted to determine the relative ignition properties of the various forms of discharge. If an ordinary inductor discharge consists of the capacity components and the fluctuating inductance components, it is possible with sufficient capacity, by adding a capacity to the secondary circuit, to cause only a single capacity spark to pass. It can then be shown by calorimetric measurements (cf. Taylor-Jones, quoted page 347) that, under various circumstances, the total energy remains the same, assuming equal conditions in the primary circuit. Such experiments on spark ignition were carried out by Morgan<sup>3</sup> showing that, with increased capacity in the secondary circuit, the ignition properties of the spark increase, and ignition therefore seems to depend only on the capacity components.

These results were regarded by Taylor-Jones and Morgan and Wheeler<sup>4</sup> as confirming a purely thermal theory, since a larger volume of gas can be heated to "ignition temperature" by a momentary source of heat than by a source effective over a longer time but of the same total output. However, an assumption of this kind is highly implausible, as was early pointed out by Finch.<sup>5</sup> That would mean that the total energy available in a spark could become chemically effective only if it were present in the most depreciated form, that of heat energy; whereas ionization, molecule stimulation, and splitting take place to a considerable degree before the energy is changed into heat.

**2. Finch's Investigations on the Reactions of Explosive Mixtures with Discharges That Do Not Lead to Ignition.**—Most observations contradict the assumption that ionization plays a deciding role. On the basis of the findings reported in the foregoing on chain reactions and explosions, we should reasonably expect that stimulus and especially dissociation are the essential elements in the discharge, in addition to which thermal effect and ionization can of course also play a role. Since it is known that atomic hydrogen produced is extraordinarily capable of reaction in a discharge and also stimulates the ignition of oxygen-hydrogen, it would be reasonable to assume that, when a spark passes through oxygen-hydrogen, a similar reaction takes place, accompanied,

<sup>1</sup> The first pictures with a rotating mirror were made by B. Walter, *Ann. Physik*, **66**, 636 (1898).

<sup>2</sup> Quoted p. 347.

<sup>3</sup> MORGAN, J.D., "Principles of Electric Spark Ignition," 1920.

<sup>4</sup> TAYLOR-JONES, quoted p. 347. TAYLOR-JONES, E., J.D. MORGAN, and R.V. WHEELER, *Phil. Mag.*, **43**, 359 (1922).

<sup>5</sup> Cf. BRADFORD and FINCH, cited p. 347.

of course, by other processes. An insight especially into these processes is afforded by the systematic investigations that Finch and his associates<sup>1</sup> performed on the nonexplosive conversion by gas discharges in explosive mixtures at low pressures. Finch and Cowen<sup>2</sup> have shown that high-tension discharges of  $\sim 600$  volts and up to  $\sim 5 \mu\text{amp}$  can be passed through oxygen-hydrogen mixtures of 30 to 90 mm pressure and electrode separation of several millimeters without ignition resulting.

For purposes of clarification, a few remarks on the nature of glow discharge should be made. The illumination phenomena appearing in a low-pressure gas discharge are sketched in Fig. 178. The essential parts include a glow membrane connected to the cathode (first cathode layer) and separated from the negative glow light by a dark space. The negative glow light is once more separated from the "positive

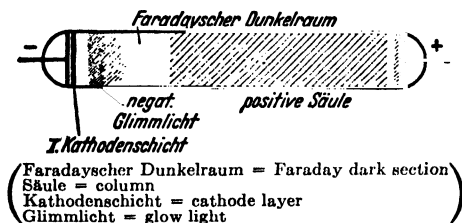


FIG. 178.—Glow discharge, schematic.

column" by a dark space, the "Faraday dark space." If the distance between the electrodes is shortened, only the positive column is at first shortened until it finally disappears altogether. If such a discharge burns in oxygen-hydrogen and if the length of the positive column is reduced, the conversion is correspondingly reduced. From this, it follows that a conversion takes place in the positive column. A further decrease of the electrode distance after the positive column has disappeared is made at the expense of the Faraday dark space and leaves the combustion velocity unchanged. From this, it further follows that combustion takes place only in the luminous portions of the discharge, in other words, in those parts in which also molecule stimulation, ionization, and dissociation take place. The combustion velocity in a discharge without a positive column is directly proportional to the current intensity but depends considerably on the material of the cathodes. A dry mixture of  $2\text{CO} + \text{O}_2$  burns three times faster at a silver cathode, for example, than at a copper cathode. Finch therefore concludes that the combustion is limited to the cathode zone.

<sup>1</sup> Cf. BRADFORD and FINCH, quoted p. 347, as well as FINCH and associates, *Proc. Roy. Soc. London*, A, **111**, 257 (1926); **116**, 529 (1927); **124**, 303, 532 (1929); **129**, 314, 656, 672 (1930); **133**, 173 (1931); **134**, 343 (1931); **143**, 282 (1934); *J. Chem. Soc.*, 1934, p. 360.

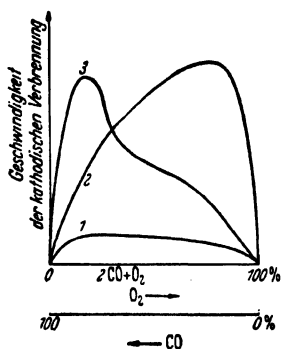
<sup>2</sup> FINCH, G.J., and L.G. COWEN, *Proc. Roy. Soc. London*, A, **111**, 257 (1926).

In Table 63 from Finch and his associates,<sup>1</sup> we present several numerical values to illustrate the quantitative aspect. Here the quotient  $c/i$  is given in dependence on the other conditions, and the entities are as follows:  $c = \text{cm}^3$  oxygen-hydrogen (under normal conditions) burned per minute, and  $i$  the current intensity in  $\mu\text{amp}$ . In special experiments, it

TABLE 63.—CATHODE COMBUSTION OF  $2\text{H}_2 + \text{O}_2$  AT VARIOUS CATHODES (FROM FINCH AND ASSOCIATES)  
Expressed in  $c/i$ , See the Text

| Gas pressure,<br>mm Hg | $2\text{H}_2 + \text{O}_2$ ( $\text{P}_2\text{O}_5$ -dry) |      |      |      | $2\text{H}_2 + \text{O}_2 +$<br>1.6 mm $\text{H}_2\text{O}$ |      | $2\text{H}_2 + \text{O}_2 +$<br>3.7 mm $\text{H}_2\text{O}$ |      |
|------------------------|---|------|------|------|---|------|---|------|
|                        | Wo  | Ta   | Ag   | Au   | Ta  | Au   | Ta  | Au   |
| 90                     | 0.38  | 0.28 | 0.27 | 0.25 | 0.32  | 0.26 | 0.34  | 0.26 |
| 60                     | 0.37  | 0.27 | 0.26 | 0.24 | 0.30  | 0.26 | 0.34  | 0.25 |
| 30                     | 0.36  | 0.26 | 0.25 | 0.23 | 0.29  | 0.25 | 0.33  | 0.24 |

was determined that, of the burned gases, up to 1.33 per cent (at Ta) or 0.75 per cent (at Au) appeared as  $\text{H}_2\text{O}_2$ . There is little to prevent the assumption that the reaction proceeds similarly to oxygen-hydrogen



(Geschwindigkeit der kathodischen Verbrennung = velocity of cathodic combustion)

FIG. 179.—Reaction of  $\text{CO} + \text{O}_2$  in glow discharge. 1. Dry at a nonatomizing cathode. 3. Damp at a nonatomizing cathode. 2. Dry at an atomizing cathode. (From Bradford and Finch, p. 341.)

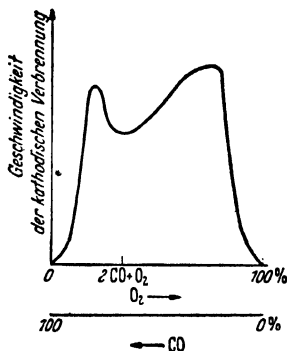


FIG. 180.—Reaction of damp  $\text{CO} + \text{O}_2$  in glow discharge at an atomizing cathode (corresponding approximately to the overlapping of curves 2 and 3 in Fig. 179). (From Bradford and Finch, p. 341.)

combustion under the influence of H-atoms. In the experiments given in the table, the conversion per unit of current is almost independent of the gas pressure and does not vary greatly with the nature of the cathode material. Nevertheless, differences exist, especially in dry gas; *e.g.*, conversions are smaller at an atomizing cathode (like silver) than at a nonatomizing cathode like Wo or Ta. The situation is just the reverse in

<sup>1</sup> FINCH, G.I., and E.A.J. MAHLER, *Proc. Roy. Soc. London, A*, **133**, 173 (1931).

carbon monoxide (*cf.* above). We illustrate with several diagrams from Finch and his associates (Figs. 179 and 180).

If we compare CO combustion at atomizing and nonatomizing cathodes, it is perhaps not surprising that the velocity at the former is many times that of nonatomizing cathodes. The velocity maximum at the atomizing cathode is on the oxygen-rich side. Water vapor accelerates combustion almost to the same maximum value as an atomizing cathode, but the velocity maximum lies on the opposite side, namely, that of high CO concentrations. If both atomizing cathodes and water vapor are allowed to work, essentially both influences make themselves felt with only relatively small mutual disturbances. We have two maxima of the velocity in dependence on the composition at those places where there were formerly individual maxima. Finch tries to explain the observed phenomena by assuming the following processes (*cf.* pages 352ff.):

1. Reaction of dry  $\text{CO} + \text{O}_2$  mixtures in the absence of metal atoms:
  - (a)  $2\text{CO} \rightarrow \text{CO}_2 + \text{C}$
  - (b) C burns with  $\text{O}_2$
2. Dry  $\text{CO} + \text{O}_2$  in the presence of metal (Me) atoms:
  - (a)  $\text{Me} + \frac{1}{2}\text{O}_2 \rightarrow \text{MeO}$
  - (b)  $\text{MeO} + \text{CO} \rightarrow \text{CO}_2 + \text{Me}$
3. Wet  $\text{CO} + \text{O}_2$ :  
 $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$

Of these processes, 3 should probably be so interpreted that the same kind of combustion takes place as usual with CO in the presence of  $\text{H}_2\text{O}$ , *i.e.*, essentially perhaps with the aid of OH-radicals (*cf.* pages 343ff.). In agreement with this is the further observation by Finch that, in  $\text{CO} + \text{O}_2 = \text{H}_2$  mixtures at atomizing and nonatomizing cathodes, the CO is favored in combustion; for, if the  $\text{H}_2$  combustion takes place by way of OH and an H is again formed each time by the reaction of OH with CO, this cannot be surprising. In addition, a direct reciprocal effect of CO with  $\text{H}_2\text{O}$  is naturally not excluded even though reaction by the mediation of OH seems to be more plausible.

The reactions assumed under 2 do not appear improbable in this or a similar manner. The effect of metal compounds as antiknocks might also consist of a taking up or giving off of oxygen by the metal originating from disintegration. It is therefore also not surprising if the atomized metal has a chain-breaking effect and if therefore the oxygen-hydrogen combustion is slower at atomizing cathodes than at nonatomizing cathodes. The reaction under 1 assumed by Finch seems less likely to us; a participation of O-atoms appears more probable. However, without direct experiments we can deal only in suppositions.



The already mentioned  $\text{CO} + \text{O}_2$  combustion in the presence of  $\text{H}_2$  does not have the characteristics of the reaction without  $\text{H}_2$  but takes a much more rapid course and rather resembles the reaction of  $\text{H}_2 + \text{O}_2$ . This too is not very surprising in view of reaction-kinetic data. In Fig. 181, the cathodic combustion velocity of  $\text{H}_2 + \text{O}_2$  as well as of  $\text{CO} + \text{H}_2 + \text{O}_2$  mixtures is plotted as a function of the fuel and oxygen content. At the atomizing cathode, a maximum is obtained for  $\text{H}_2 + \text{O}_2$  on the  $\text{H}_2$ -rich side. For nonatomizing cathodes (tantalum), the reaction velocity continues to rise with increased fuel content as well for  $\text{H}_2 + \text{O}_2$  as for  $\text{CO} + \text{H}_2 + \text{O}_2$ , and it has not reached its maximum in  $\text{H}_2$ - $\text{O}_2$  mixtures even at 99.5 per cent of  $\text{H}_2$ .

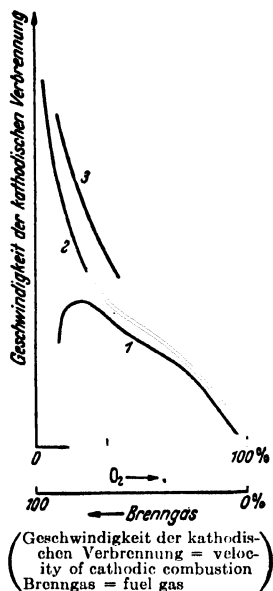


FIG. 181.—Reaction of  $\text{H}_2$  with  $\text{O}_2$  in glow discharge; at atomizing cathode, 1; at nonatomizing cathode, 2; reaction of  $\text{CO} + \text{H}_2$  with  $\text{O}_2$  at nonatomizing cathode, 3. (From Bradford and Finch, p. 341.)

velocity continues to rise with increased fuel content as well for  $\text{H}_2 + \text{O}_2$  as for  $\text{CO} + \text{H}_2 + \text{O}_2$ , and it has not reached its maximum in  $\text{H}_2$ - $\text{O}_2$  mixtures even at 99.5 per cent of  $\text{H}_2$ . In  $\text{CO} + \text{H}_2 + \text{O}_2$  mixtures, the favored combustion of carbon monoxide is more decided at atomizing than at nonatomizing electrodes, even though the total velocity at the atomizing cathode can be smaller. Finch concludes from this that it might be two different oxidation products of water that come into play in  $\text{CO}$  combustion, of which one is richer in oxygen than the other, and that metal atoms either hinder the formation of the more oxygen-rich product or accelerate its destruction. In this manner, they are thought to increase the amount by which the  $\text{CO}$  is favored in combustion, while at the same time they decrease the total oxidation velocity. Since  $\text{H}_2\text{O}_2$ , even though it can be shown to be present in small quantities, is improbable as an intermediate product,  $\text{OH}$  is suggested as a possible oxygen transmitter, which is probable after what has been said above. Finch therefore suggests the following

for  $\text{CO} + \text{H}_2$  combustion at the nonatomizing cathode:

- (a)  $\text{H}_2$  burns, by way of  $\text{OH}$ , to  $\text{H}_2\text{O}$
- (b)  $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$
- (c)  $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$

Of these, the third once more appears to us as the least likely reaction. Finch assumes that  $\text{Me}$ -atoms inhibit the formation of  $\text{OH}$  as an intermediate product of the  $\text{H}_2$  combustion. It should also be considered as a possibility, however, that the  $\text{Me}$ -atoms stimulate the recombination of  $\text{H}$ -atoms, which is almost certainly the case. At least the decrease

in the reaction velocity of  $H_2$ -containing mixtures at atomizing cathodes could readily be explained in this manner. Perhaps also the decrease of participation of  $H_2$  in the combustion could be explained by a favored reverse formation of  $H_2$  in the triple collision or after intermediary formation of  $MeH$ . In addition, of course, a participation of  $HO_2$  is conceivable (*cf.* pages 317ff.).

The dependence of the oxidation velocity on the concentration does not seem to us easy to explain. Finch assumes that  $H_2$  as well  $O_2$  must be stimulated, that the life of the stimulated  $H_2$  is much longer than that of  $O_2$ , and that the velocity on the  $H_2$ -rich side at nonatomizing electrodes therefore rises so sharply. It appears to us that more detailed investigations on the manner of the stimulation would be necessary. Since H-atoms are formed profusely in the discharge from  $H_2$ , it would seem most logical to make H-atoms responsible for the reaction in the discharge too, and this is also in agreement with other kinetic facts. If we assumed that O-atoms would be formed only in a subordinate degree and that especially stimulated  $O_2$ -molecules would be formed, which naturally have a shorter life than the H-atoms, then we should arrive at Finch's assumption. It is not immediately clear, however, why O-atoms should not be formed in greater concentration since the dissociation heat (117 kcal) is not so very much greater than that of  $H_2$  (102.5 kcal).

The conclusion by Finch that, in dry  $H_2$ - $O_2$  mixtures at nonatomizing electrodes, the reaction  $H_2 + O_2 \rightarrow 2OH$  is determining and on the other hand that, in the presence of moisture, the reaction  $2H_2O \rightarrow 2OH + H_2$  is determining can be accepted to the extent that in both cases it depends on OH formation; but the special mechanism must remain undetermined. In the presence of Me-atoms, the reaction  $Me + \frac{1}{2}O_2 \rightarrow MeO$ ;  $H_2 + MeO \rightarrow H_2O + Me$ , as it is suggested by Finch, need probably not be the only one coming into consideration.

The main reason that the participation of H- or O-atoms is not assumed by Finch is that, in special experiments in which  $H_2$  or  $O_2$ , or both separately, had previously gone through a discharge and then were mixed, only a small reaction could be shown to have taken place. Furthermore, H-atoms in greater quantities originate in negative glow light only in wet  $H_2$ ; but, in the presence of  $O_2$ , the conditions for this will always have to be regarded as given. That the reaction is small in subsequently mixed gases can very well be due to the fact that, up to the point of mixing, the concentration of the active particles has diminished considerably. Particularly the oxygen atoms at the relatively high pressures applied are quickly combined, forming ozone which on its part is at low temperatures (as soon as it has lost its initial energy) by far not so active as the former (*cf.* page 319). By this means, the apparent contradiction between Finch's experiments and the usual data

on the reactions of the free H- and O-atoms could perhaps be eliminated. If, however, the free atoms originate directly in the mixture of both gases, the conditions for reaction are essentially more favorable. Particularly the relation of the probabilities for the reaction of O with  $H_2$  and the destruction of O in triple collision with  $O_2$ -forming ozone would have to be more favorable the higher the ratio  $H_2:O_2$ . Whether the sharp increase of the reaction velocity in  $H_2$ - $O_2$  mixtures at nonatomizing cathodes with increasing  $H_2$  content is explained by this could likewise be decided only by further experiments.

**3. Experiments on the Ignition Properties of Various Sparks as Well as of the Various Components of a Spark.**—For ignition by direct current discharges in the experiments by Finch and Cowen already mentioned, a hyperbolic relation between the gas pressure  $p$  and the current necessary for ignition  $i$  has resulted over a rather wide range; hence  $p \cdot i = \text{const.}$  Among the questionable conditions, *i.e.*, constant drop in potential in the discharge, the concentration of ions or stimulated molecules or atoms is likewise approximately a hyperbolic function of the gas pressure. For this reason, Finch concludes that, under the conditions of his experiments, ignition was determined by the reaching of a certain concentration of suitably stimulated molecules or atoms. It is probably not possible to ignore completely the thermal effect of the discharge, since relatively small rises in temperature are already of considerable effect on the reaction velocity. For the participation of ions in ignition, no data are available, even though they cannot be excluded with certainty. To be sure, spectroscopic investigations<sup>1</sup> show that, in discharges by means of CO or  $2CO + O_2$ , as well with atomizing as nonatomizing electrodes, in the positive column and in the cathode column, CO bands are present, although there was no indication of ionized CO. If it is assumed that not stimulated CO but stimulated or dissociated oxygen induces the reaction, this observation permits of no further conclusions.

With minor reservations, however, we shall agree with Finch's conclusion that ignition depends on a sufficient concentration of suitably activated molecules (by which we mean also free atoms). The following experiment was executed as a test case: Mixtures of  $2CO + O_2$  were ignited by means of condenser discharges of known oscillation frequency. The frequency was varied and independently of it the entire conducted energy, or conduction per unit of time (or conduction during the first half period). The minimum pressure was taken as the measure of the ignition properties; *i.e.*, the ignition properties were plotted as inversely proportional to the minimum ignition pressure. The ignition values obtained with this apparatus for various values of the capacity

<sup>1</sup> FINCH, G.J., and THOMPSON, *Proc. Roy. Soc. London, A*, **129**, 314 (1930).

in the oscillation cycle and various total energies are given in Fig. 182. In it, the peak current is also plotted at  $C = 0.041 \mu\text{f}$ , which takes an analogous course in other capacities. The results show the following: The frequency of the discharge exercises a much more decided influence than the energy. The ignition quality increases considerably with decreasing frequency, although the energy given off decreases at the same time. The ignition quality was by no means determined by the value of the peak current, which takes a course opposite to that of the former. The observations exclude any purely thermal explanation. They merely show that the stimulus conditions are varied under varied circumstances. It is known that the stimulus levels in a condenser discharge are higher as their frequency is higher. The high-frequency discharge generally yields many ions, whereas the discharge with lower frequency yields more neutral atoms and stimulated molecules. In agreement with other experiences, it should therefore be concluded that the latter and not ions are determining for ignition.

Spectroscopic investigations of ignition sparks by Yumoto<sup>1</sup> yielded results like those of Finch: The ignition properties of sparks are greater under conditions in which band spectrums appear than under conditions in which spark spectrums appear. With longer sparks (in air), those parts are most effective in which  $\text{N}_2$  or  $\text{N}_2^+$  bands appear (which of course have nothing to do with ignition).

It now remains to discuss those experiments which are carried out on the effectiveness of the various components of an inductor discharge. Finch's and Sutton's oscillographic investigations of inductor sparks have already been mentioned. It was important to experiment separately with the individual portions of the discharge, namely, the oscillating capacity component of very short duration ( $\sim 10^{-6}$  sec), of high frequency ( $\sim 10^7$ ), and of high maximum current intensity ( $> 10$  amp) and the inductance components of the same current direction, but with superimposed oscillations of low frequency (e.g.,  $\sim 10^4$ ) and longer total duration, of the order of magnitude  $\sim 10^{-3}$  sec and of very much smaller maximum intensity (e.g.,  $< 0.1$  amp), whose total production can under certain circumstances be just as great as or greater than that of the capacity

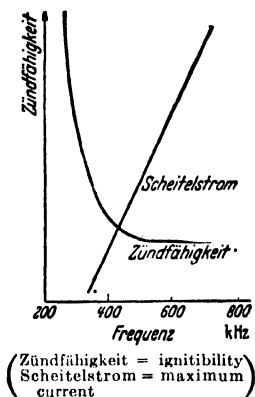


FIG. 182.—Influence of the frequency and maximum current of a discharge on its ignitability (maximum current plotted for  $0.041 \mu\text{f}$ ). See the text. (From Bradford and Finch, p. 341.)

<sup>1</sup> YUMOTO, K., *Sci. Papers Inst. Phys. Chem. Research Tokyo*, **21**, 254 (1933).

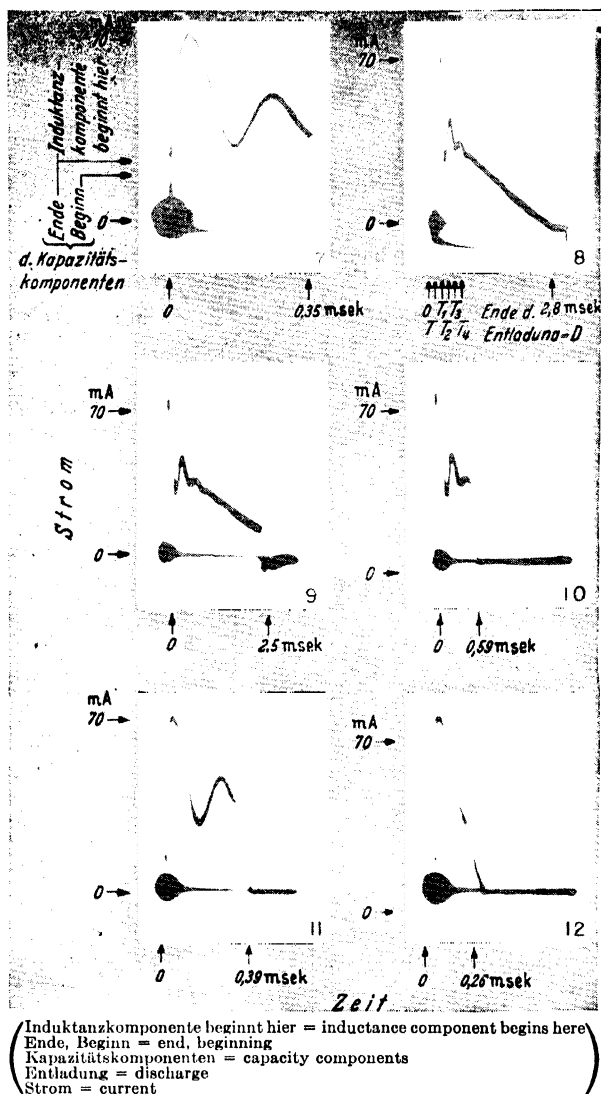


FIG. 183.—Oscillograms of inductor discharges: picture 7, with condenser parallel to the spark gap; 8, complete discharge; 9, late interruption of the discharge; 10, interruption at  $T_1$ ; 11, interruption at  $T_2$ ; 12, interruption at  $T_1$  (time scale different from picture to picture.) (From Bradford and Finch, p. 341.)

components because of the longer duration. Finch and his associates<sup>1</sup> did this in the following manner: By using a glow cathode tube with a suitable saturation current in the region of discharge, it was possible

<sup>1</sup> BRADFORD, B.W., G.J. FINCH, and Miss A.M. PRIOR, *J. Chem. Soc.*, 1933, p. 227; 1934, p. 75. FINCH, G.J., and R.W. SUTTON, *Proc. Phys. Soc. London*, **45**, 288 (1933).

to suppress the capacity component practically completely while the inductance component passed through uninfluenced. To suppress the inductance component at the desired intervals, a special double interrupter was built with which the primary circuit could again be closed after interruption in various very short intervals, by which, as was shown theoretically and experimentally, the spark is directly broken off. Amplitude and frequency of the inductance components are regulated by changing the primary current and capacity.

Several typical results by Finch and his associates are given in Table 64; they refer to  $2\text{CO} + \text{O}_2 + 5$  per cent  $\text{H}_2$ . The points of time at the end of the discharge refer to the oscillograph (Fig. 183, picture 8, end of the discharge  $T_4$ ,  $T_3$ ,  $T_2$ ,  $T_1$ ,  $T$ ; cf. in this connection pictures 9, 10, 11, and 12).

From the data of Table 64, it is clear that an essential part of the ignition is due to the inductance component. Individual differences

TABLE 64.—INDUCTOR IGNITION AND INDUCTANCE COMPONENT IN A MIXTURE OF  $2\text{CO} + \text{O}_2 + 5$  PER CENT  $\text{H}_2$  (FROM BRADFORD, FINCH, AND PRIOR)

| Energy of the inductance component, m joule | Duration of the inductance components, m sec | Ignitibility = 1000: minimum ignition pressure, mm <sup>-1</sup> Hg | Minimum ignition pressure, mm Hg |
|---|--|---|----------------------------------|
| 20.5  | 2.81   | 9.43  | 106                              |
| 9.2   | 0.79   | 7.70  | 130                              |
| 7.4   | 0.59   | 7.41  | 149                              |
| 5.2   | 0.39   | 6.50  | 154                              |
| 2.4   | 0.20   | 5.13  | 195                              |
| ~ 0.15                                      | 0.02   | 4.26  | 235                              |

from material to material are noted in this respect.  $2\text{H}_2 + \text{O}_2$  and  $\text{CH}_4 + \text{O}_2$  showed analogous results, but in the latter case the cutting off of the inductance components had a much smaller influence on the ignition properties of the discharge.

In further experiments, the ignition properties of sparks were investigated; and, in addition to the effect of the capacity components, also that of the peak value of the current as well as the duration of the inductance components were established.

The conditions of the discharge are presented in Table 65, taken from Finch.

A comparison of experiments B and C shows that cutting out the capacity components had an unusually small effect on the ignition properties. If, on the other hand, only the inductance component was cut out, the capacity component did not suffice for ignition in  $2\text{CO} + \text{O}_2 + 5$  per cent  $\text{H}_2$  at the highest pressures that could be applied without

TABLE 65.—DISCHARGE CONDITIONS (FROM FINCH)<sup>1</sup>

|  |  |
|--|--|
| A. —   | Normal inductor discharge  |
| B. Glow cathode tube in series with spark gap; condenser parallel with it; glow cathode fully heated | Normal inductor discharge  |
| C. With glow cathode tube, without condenser:  |  |
| a. Cathode fully heated  | Negligible capacity component; inductance component uninfluenced   |
| b. Cathode slightly heated   | Negligible capacity component; normal (or almost normal) duration of the inductance component; oscillations more or less subdued |
| D. Condenser parallel with glow cathode tube; cathode cold   | Normal capacity component; negligible induction component  |
| E. As before, without condenser  |  |

<sup>1</sup> An oscillograph of these discharges appears in the original.

danger. In the case of  $\text{CH}_4 + \text{O}_2$ , ignition was still possible but at greatly increased pressure.

TABLE 66.—RESULTS WITH NORMAL DURATION OF THE INDUCTANCE COMPONENTS (FROM FINCH)

Conditions for Discharge in Table 65

| Discharge | Minimum ignition pressure, mm Hg           | Ignitibility | Energy of the capacity component, m joule | Inductance component |                 |
|-----------|--|--------------|---|----------------------|-----------------|
|           |  |              |   | Energy, m joule      | Duration, m sec |
|           | $2\text{CO} + \text{O}_2 + 5\% \text{H}_2$ |              |   |                      |                 |
| A         | 92.5                                       | 10.8         | 0.62                                      | —                    | —               |
| B         | 108.0                                      | 9.3          | 0.84                                      | 29.8                 | —               |
| C (a)     | 111.0                                      | 9.0          | 0.89                                      | —                    | —               |
| D         | No ignition at 304.0                       | 3.3          | 6.7                                       | —                    | —               |
| E         | No ignition at 313                         | 3.2          | 7.1                                       | —                    | —               |
|           | $\text{CH}_4 + \text{O}_2$                 |              |   |                      |                 |
| A         | 89.5                                       | 11.2         | 0.58                                      | 23.8                 | 2.67            |
| B         | 90.5                                       | 11.1         | 0.59                                      |                      |                 |
| C (a)     | 92.0                                       | 10.8         | 0.61                                      |                      |                 |
| D         | 224  | 4.5          | 3.6                                       | —                    | —               |
| E         | No ignition at 250                         | 4.0          | 4.5                                       | —                    | —               |

Still more impressive are experiments with reduced inductance components. Thus, for example, a  $2\text{CO} + \text{O}_2 + 5$  per cent  $\text{H}_2$  mixture of 152 mm Hg still ignited at a duration of the inductance component of 0.38 m sec and an energy of 5.11 m joule, whereas a capacity compo-

ment of 8.8 m joule did not suffice for ignition even at 350 mm. From the experiments, it is clear that the ignition properties of a normal inductance component can be stimulated only a little by the preceding capacity component in an induction discharge.

For further details on spark ignition of various mixtures, we refer the reader to Bradford and Finch (quoted pages 347, 349).

**4. Other Observations on "Nonthermal" Ignition in Sparks and Discharges.**—The fact that spark ignition is not a thermal phenomenon is attested, among other sources, by observations from Semenov's Institute. As has partly been discussed (page 304), the explosion limits of many systems are extended, or the minimum ignition tempera-

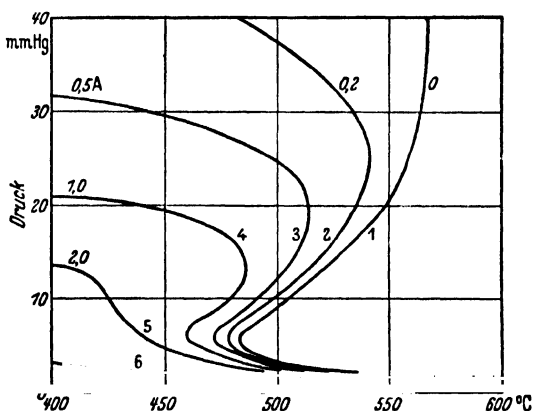


FIG. 184.—Explosion ranges of  $2\text{H}_2 + \text{O}_2$  for auto-ignition, 1, as well as under the influence of various discharges (intensity of the primary current of the transformer used as measure), Gorschakov and Lavrov. (From Semenov.)

tures lowered, if free atoms are introduced (*e.g.*, from a discharge or by illumination). Something similar is noted if a spark is allowed to pass through the mixture itself. Kowalsky<sup>1</sup> and later Gorschakov and Lavrov<sup>2</sup> determined the ignition limits of oxygen-hydrogen mixtures for sparks of varied energy (low-frequency sparks of a transformer; as a measure for the spark intensity, the intensity of the primary current in the transformer was used). As was to be expected, the ignition temperature is decreased as the spark becomes more intense; in the proximity of the explosion limits,<sup>3</sup> very weak sparks suffice for ignition. For temperatures above  $500^\circ\text{C}$ , there is only a lower ignition limit. This means, therefore, that, at gas pressures that do not suffice to induce a spontaneous chain explosion at the temperature in question, no explosions can be forced by sparks either. At somewhat higher pressures, the

<sup>1</sup> KOWALSKY, A., *Z. physik. Chem.*, Sec. B, II, 56 (1930).

<sup>2</sup> GORSCHAKOV, G., and F. LAVROV, *Acta Physicochim. URSS*, 1, 139 (1934).

<sup>3</sup> By this is meant the pressure limits for auto-ignition (*cf.* p. 13).



influence of the spark becomes very great, however (cf. Fig. 184), and it becomes greater the greater the current intensity. It is worthy of note that, at not too high current intensities (several tenths of an ampere primary), an upper ignition limit is still preserved and that therefore no basic difference exists in the ignition phenomena between weak sparks and spontaneous ignition. The same is true if instead of a spark a quiet electrode-less discharge is used. In this case too, there are upper and lower ignition limits, but the ignition range is enlarged<sup>1</sup> (at the lower limit measured not above 450°). These results appear very plausible. Nevertheless, it must be emphasized that they cannot be expected according to Semenoff's theory in its original form, for the expression of the reaction velocity

$$v \sim \frac{n_0}{\beta - \delta}$$

yields explosions only for  $\beta = \delta$ , not for an increase of  $n_0$ . The reaction velocity can, of course, be increased so much by increasing  $n_0$  that no heat equilibrium exists any more and explosion therefore takes place. This is an entirely possible process, which probably must be drawn upon as an explanation in many cases (Chap. VIII, page 278), but doubtless not in all; for, where so-called "cold flames" appear, the disturbance of the heat equilibrium certainly cannot have been the cause of the explosion. Formally, the relations can easily be expressed by the hypothesis of "chain interaction" by which Semenoff,<sup>2</sup> as mentioned on page 279, means the following: The expression for chain-branching contains a member that depends on the square of the concentration of the active particles. As a result, the chain-branching is increased by increasing this concentration, and explosion can be forced. Formally, this is correct. However, it is in general not easy actually to find a reaction that, in respect to the active particles, is of the second order and furnishes chain-branching. As has been explained in detail, it will be permissible to regard the condition only if in addition to the formal relation we can show the real reactions that represent chain interaction. That explosion can be obtained by strict computation even without chain interaction if several of the omissions undertaken by Semenoff are given up has been shown in the meantime<sup>3</sup> (cf. in this connection Chap. VIII, pages 278ff.).

**5. Spark Ignition in the Engine.**—Finch and Mole<sup>4</sup> also carried out experiments on the influence of the inductance components on ignition

<sup>1</sup> DUBOWITSKY, NALBANDJAN, and N. SEMENOFF, *Trans. Faraday Soc.*, **29**, 606 (1933).

<sup>2</sup> SEMENOFF, N., "Chemical Kinetics and Chain Reactions"; also, *Phys. Z.S.U.*, **1**, 725 (1932); *Z. physik. Chem.*, Sec. B, **28**, 44 (1935).

<sup>3</sup> JOST, N., and L. v. MÜFFLING, *Z. physik. Chem.*, Sec. A, **43**, 183 (1938).

<sup>4</sup> FINCH, G.J., and G. MOLE, *Trans. Inst. Automob. Engrs.*, 1934, p. 71.

in an engine. In the engine, the conditions are essentially different from those in the original experiments by Finch, where room temperature and pressures of not more than about 0.2 atm prevailed; whereas in the engine the pressures are considerable and the temperatures at the end of the compression stroke reach several hundred degrees centigrade. In the engine, a spark of such great energy is used that ignition surely results even if only the capacity component is present. The experiments yielded the following: Output, efficiency, and speed of the engine remained unchanged, if the inductance component was cut so far that its duration dropped from 2 to 0.5 m sec. Also, a variation in the peak value of the secondary current in the inductance component was without influence on the running of the engine. With sufficient shortening of the spark duration, misfiring occurred; the cause of this turned out to be that the spark occasionally could not jump the spark gap of the spark plug, and not that a spark could not ignite the mixture. In practical engine operation, the capacity component alone suffices for ignition.

**6. Brewer's Investigations on Reactions as the Result of Discharges in Nonexplosive and Explosive Mixtures.**—We want to discuss the works of Brewer<sup>1</sup> separately, since they are not directly comparable with those of Finch because of the somewhat different experimental conditions, although they partly confirm the findings of Finch.

Brewer, in general, worked at lower pressures than Finch (0.2 to 20 mm Hg). Over this interval, the reaction in nonexplosive mixtures is found to be independent of the pressure, from which it is concluded that definite reaction centers but not ranges of especially high energy play a role; likewise, that no dissociation equilibriums or addition reaction equilibriums, which are dependent on the pressure, can take part. The reaction velocity is proportional to the current as in Finch. From the intensities of the spectrums, it is concluded that the concentration of atoms and stimulated molecules depends on the pressure and the density of the current, which direct measurements of the atom concentration by Crew and Hulburt<sup>2</sup> confirm. On the other hand, the velocity of the production of positive ions should be independent of the pressure and proportional to the current, and Brewer therefore assumes that positive ions are the primary reaction centers. Further experiments will have to show in how far this conclusion, which contradicts other views, can be maintained.

The finding is noteworthy that, in nonexplosive mixtures, reactions in the glow discharge take place with a temperature coefficient  $\leq 0$ . Even the  $\text{H}_2$  oxidation does not change its velocity over an interval of

<sup>1</sup> BREWER, KEITH, A., A comprehensive presentation, *Chem. Rev.*, **21**, 213 (1937); *J. physik. Chem.*, **33**, 883 (1929) to **35**, 1051 (1934); *J. Am. Chem. Soc.*, **53**, 2968 (1931).

<sup>2</sup> CREW and HULBURT, *Phys. Rev.*, **30**, 124 (1937).

400°C. Just as noteworthy is the influence of added foreign gases. In the reaction of gas mixtures, the velocity generally rises by increasing the concentration of the components with the higher ionization potential. Added foreign gases (with the exception of helium with an especially high ionization potential of 24.5 volts) inhibit the reaction, whereas He accelerates it. Brewer concludes that ions of the components with the lower ionization tension as well as ions of foreign gases are relatively ineffective in inducing reaction. Perhaps we can also interpret these findings in such a way that the production of free atoms is decreased as more gases with a low ionization tension are present that can easily take up the energy.

The foregoing findings referred to nonexplosive mixtures; in explosive mixtures, certain factors change. Here the reaction velocity is in general accelerated by the addition of inactive gases. Since diffusion phenomena apparently play a part, the assumption of one of the usual atom reactions would be possible. The differences that appear in the action of explosive and nonexplosive mixtures probably point to the fact that ions participate in the latter; whereas, in the former, the assumption of free atoms and radicals as reaction agents suffices. In explosive reactions, Brewer also finds the greater dependence on temperature and pressure that is to be expected.

### 7. Expressions for the Theory of "Nonthermal" Ignition in the Spark.

Of the attempts at a theoretical treatment of spark ignition, two works deserve special mention.<sup>1</sup> The work by Mole furnishes a mathematical formulation of Finch's activation theory of spark ignition and is based on an analogy between the action of activated particles that participate in ignition and that of gas ions that recombine. The method that Langevin<sup>2</sup> applied to the latter is therefore transferred to the former. Two different active particles are at first assumed, corresponding to positive and negative ions (Mole constantly speaks of activated molecules, although his computation really fits the case of free atoms). Thus two simultaneous nonlinear differential equations result, whose solution is easily possible if we assume the concentration of both types of active particles as being equal. We therefore arrive at the same conclusion if from the outset only one type of active particle, perhaps free atoms, is assumed. The differential equation for the change in time of their concentration is

$$\frac{dn}{dt} = a + bn^2 - cn \quad (1)$$

In this,  $a$  gives the number of the artificially produced active particles in a unit of time, in other words, in a spark.  $-cn$  is to be the velocity

<sup>1</sup> MOLE, G., *Proc. Phys. Soc. London*, **48**, 857 (1936). LANDAU, H.G., *Chem. Rev.*, **21**, 245 (1937).

<sup>2</sup> LANGEVIN, *Ann. chim. phys.*, **28**, 433 (1903).

of the spontaneous fading of stimulated molecules. If we are thinking of free atoms instead of stimulated molecules (as the recombination introduced by Mole really demands), however, this member could be interpreted as the velocity of the deactivation by diffusion to the wall. The coefficient  $b$  is, according to Mole,

$$b = \alpha(mj - 1)$$

in which the first member measures the activation as a result of the energy liberated in recombination, and the second measures the deactivation by recombination. Mole assumes it to be self-evident that  $b > 0$ ; although we are of the opposite opinion, we shall give the results that follow from Mole's assumption  $a, b, c > 0$ . With  $b > 0$ , the differential equation (1) is identical with that which we should obtain according to Semenov by introducing chain interaction (branching  $\sim n^2$ ) under the assumption that this branching of the second order is so strong that we can disregard that of the first order. This case, then, is referred to by the integrals that Mole gives for various assumptions regarding the constants. If we wish to investigate that sort of relation, Mole's expressions can be applied with benefit.

However, we raise the basic objection that probably  $b < 0$ , and then, as has already been discussed (*cf.* page 278), a static concentration must always appear and no explosion results. The assumption  $b > 0$  assumes that, in recombination, which combines two active particles, more than two new active particles arise by secondary activation. In reality, however, only the dissociation work for a pair of free atoms is obtained in recombination; and, since the latter can be used only for the activation of new particles in a fraction of the recombination processes, more active particles must disappear by recombination than are produced. To be sure, we base this on the fact that we are dealing with free atoms, whereas Mole operates with stimulated molecules. In this case, however, it would be still less clear how the process is to take place, since no direct proofs of the participation of stimulated molecules in the reaction have hitherto been produced and since this participation is not very likely because of the generally very short life of stimulated molecules. Experiments with added gases that have a deactivating effect on the stimulated molecules might be suitable for experimental tests. Mole's investigation therefore appears to be only a starting point for attacking the problem, the solution of which it has not produced (even though it leads to very interesting conclusions), since it does not sufficiently fit the actual experimental facts.

A mathematical treatment of the ignition process which Landau (page 362) has carried out on the suggestion of Lewis and v. Elbe comes much closer to the generally accepted physical picture of these processes.

He considers a reaction in which a kind of active particle participates. To begin with, he lets a certain initial concentration of these particles be present in a small partial volume as the effect of the spark; likewise a certain temperature that is higher in respect to the remaining gas. He now imagines a reaction taking place with chain-branching and at the same time takes heat conduction and diffusion of active particles into consideration. Since it is reasonable to regard the spark volume as a sphere, we obtain for heat conduction, if the origin of the coordinate system lies in the center of this sphere,

$$\frac{\partial T}{\partial t} = k \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial T}{\partial r} \right) + \frac{Q}{c} f(n) \quad (2)$$

in which the first member to the right is the temperature change by heat conduction and the second is the temperature change as the result of heat production by chemical reaction ( $Q$  heat production per unit of conversion,  $c$  heat capacity of the unit of volume, and  $f(n)$  the reaction velocity). For the change of the concentration of active particles, we obtain correspondingly

$$\frac{\partial n}{\partial t} = k \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial n}{\partial r} \right) + \alpha n \quad (3)$$

In this, the diffusion coefficient  $k$  is equated with the temperature conductivity  $k$ , which is an allowable simplification, since both entities are always approximately equal.  $\alpha$  represents in Landau the branching coefficient;  $\alpha n$  is therefore the increase of the concentration of active particles by chain-branching (as long as we regard branching and breaking as linear in the concentration of the chain agents, we can also regard  $\alpha$  as the difference between branching and breaking; the equation is therefore that much more general than indicated by Landau). Simplifying still further, Landau writes  $f(n) = f_0 \cdot n$ , that is, the reaction velocity is proportional to the concentration of active particles, which is likewise a permissible simplification. So far, the initial equations of Landau take care of all the essential physical conditions. However, it is possible to integrate the above equations only in a relatively simple manner if  $\alpha$  is constant. For that reason, this entity is assumed to be constant by Landau, whereas in reality  $\alpha$  certainly varies exponentially and sometimes greatly with the temperature. Use is also made of the constancy of  $Qf_0$ .\*  $f_0$ , the reaction velocity, however, certainly changes exponentially and quite considerably with the temperature. For these reasons, Landau's results will have to be accepted with great caution. Nevertheless it appears that Landau has computed that case

\* In Landau,  $Qf_0$  is designated by  $Q$ !

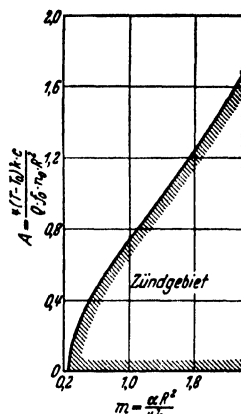
that does the greatest justice to the physical relation and, in addition, permits an integration in closed form.

A discussion of the computation would take up too much space here. We obtain a relatively simple expression for the temperature at the starting point, and it is reasonable to assume as a condition of ignition that the temperature never drops there.<sup>1</sup> The condition for this yields the following picture, which essentially represents a relation between  $\alpha$  and an expression  $A = \frac{4(T - T_0)kc}{Qf_0n_0R^2}$  if the initial condition read as follows:

$$\left. \begin{array}{ll} n = n_0 & \text{for } 0 \leq r < R \\ n = 0 & \text{for } r > R \end{array} \right\} \quad \text{and } t = 0$$

Because  $\partial T(0,t)/\partial t \geq 0$ , the relation between  $A$  and  $\alpha$  plotted in Fig. 185 results. Landau attempts to test his results by experience, for which purpose he draws upon Silver's experiments<sup>2</sup> (page 29) on ignition by hot pellets of varying radii. The test is questionable insofar as he subsequently inserts branching velocity and reaction velocity as temperature functions after he has performed the computations by assuming their constancy. The experiments, to be sure, fit the relations thus obtained, but they would have fitted another relation assumed by Silver<sup>2</sup> just as well and would fit any relation that, as its most essential factor, would give an exponential connection of the temperature with a reciprocal power of the minimum radius of the pellet necessary for ignition.

If, therefore, we do not regard this result as a support for Landau's theory but permit the objection made above to stand, Landau's treatment might nevertheless be suited as a point of departure for a more exact theory. As soon as we introduce the branching velocity as an exponential function of the temperature into the differential equation, we obtain a transcendental differential equation that can be treated only by numerical methods; but this will be necessary for a further development of the theory of ignition.<sup>3</sup>



(Zündgebiet = ignition range)

FIG. 185.—Ignition range according to the theory of Landau, p. 29; see the text.

<sup>1</sup> It is possible that the temperature rises at the beginning but then drops again; this cannot correspond to ignition, therefore.

<sup>2</sup> Cf. Chap. I, p. 31.

<sup>3</sup> For spark ignition, cf. also E. SEILER, *Brennstoff- u. Wärmewirt.*, **17**, 186 (1935). SLOANE, R. W., *Phil. Mag.*, (7), **19**, 998 (1935).

## APPENDIX

In practically all flames, a certain ionization can be proved to be present. Flame propagation can sometimes be considerably influenced by electrical fields. This influence might be understood in most cases as the result of the gas currents caused by the movement of the ions in the field. For the present, there does not seem to be any convincing reason to assume an essential participation of the ions in the chemical reactions.<sup>1</sup>

<sup>1</sup> Cf. in this connection, among others, HABER, F., *Sitzber. preuss. Akad. Wiss. Physik. math. Klasse*, 1929, p. 162. BECKER, A., "Handbuch der experimentellen Physik," Vol. XIII, 1929. WILSON, H.A., *Rev. Mod. Phys.*, **3**, 156 (1931). VOGT, K., *Ann. phys.*, **12**, 433 (1932).

Views differing from those above are represented by A.E. Malinowski and associates, *J. chim. phys.*, **21**, 469 (1924); *Z. Physik*, **59**, 690 (1930); *Phys. Z. Sovet.*, **2**, 52 (1932); **3**, 529, 537 (1933); **5**, 212, 446, 453, 902 (1934); **6**, 549 (1934); **7**, 43 (1935); **8**, 289, 536, 541 (1935); **9**, 264, 268 (1936); *Acta Physicochim. URSS*, **4**, 929 (1936).

## CHAPTER XI

### THE COMBUSTION OF HYDROCARBONS

#### SURVEY OF THE FIELD

In the oxidation of hydrocarbons, three fields can be differentiated: the catalytic oxidation, already taking place at relatively low temperatures, sometimes noticeable below  $\sim 100^{\circ}\text{C}$ ;<sup>1</sup> the slow oxidation in the gas phase in a range from about  $200^{\circ}$  to  $300^{\circ}$  to about  $500^{\circ}$  to  $600^{\circ}\text{C}$ ; and finally the explosive combustion in the flame. The range of catalytic oxidation, which is chiefly of interest from the point of view of chemical preparations, must be disregarded here. We shall deal in detail with the processes of slow oxidation at moderately high temperatures which sometimes lead to autoignition. They have been investigated most thoroughly, and they are also of special importance because, after everything that is known up to the present, they coincide with those processes which take place in the adiabatically compressed mixtures of an engine and which lead to undesirable knocking in the Otto engine and to the desired ignition in the Diesel engine. Only indirect experiments have been made on the mechanism of explosive combustion, and these will be discussed in Sec. A.

In the case of explosive combustion in the flame, free radicals might play a role. The presence of OH in every hydrocarbon flame is known from its spectrum. H-atoms are present at higher temperatures in noticeable concentration even at equilibrium. The presence of other radicals (CC, CH, and perhaps HCO) can likewise be seen from the flame spectra, even though the role of these radicals for the reaction mechanism is not as yet clarified (*cf.* Sec. A).

In slow oxidation (Sec. B, page 376) of hydrocarbons, we generally observe an autocatalytic course of the reaction even in the case of alcohols and aldehydes; *i.e.*, the reaction begins to accelerate after a certain induction period. The induction period is decreased by raising the temperature and pressure and by the presence of certain materials (in hydrocarbons sometimes by aldehydes, sometimes by peroxides, etc.), it is prolonged by other additions. (sometimes iodine, aniline, lead tetraethyl, insofar as it is given opportunity to disintegrate), it is usually

<sup>1</sup> In the liquid phase, the oxidation is sometimes noticeable at still lower temperatures, on which fact the technical application of the oxidation of paraffins for obtaining fatty acids is based. In this connection, see G. Wietzel, *Z. angew. Chem.*, **51**, 531 (1938).



dependent on the condition of the wall, and it can sometimes be absent altogether, *e.g.*, in aldehydes under not too mild conditions. As reaction products, there appear, besides CO, H<sub>2</sub>O, and usually a little CO<sub>2</sub>, great quantities of aldehydes, particularly formaldehyde, and also acids and alcohols, the latter particularly at high pressures. Often peroxides can be shown to be present in small quantities; and H<sub>2</sub>O<sub>2</sub> is sometimes the primary product and only later in the condensed reaction products (perhaps at the wall) continues to react with formaldehyde and the like to form organic peroxides (*cf.* page 406).

In the oxidation of aliphatic hydrocarbons and their oxidation products, a bluish luminescence is noted as well as the appearance of "cold flames" at low temperatures (*cf.* pages 437*ff.*) in which only a partial oxidation and no complete combustion takes place. The cold flames disappear with rising temperature, and parallel with it a "negative temperature coefficient"<sup>1</sup> of the reaction velocity is observed; *i.e.*, the velocity of the conversion decreases with rising temperature (*cf.* pages 428, 437*ff.*). In addition, the appearance of peroxides runs parallel with the appearance of cold flames; and, since phenomena corresponding to cold flames have been observed in the disintegration of peroxides (*cf.* page 463) and since, moreover, the great instability of these compounds is known, the appearance of cold flames has always been associated with the reactions of these peroxides. Even though this simultaneity may be no coincidence, somewhat varying interpretations are, under certain circumstances, possible (*cf.* pages 493*ff.*).

The oxidation stability of the hydrocarbons and their derivatives generally decreases with the increase in size of the molecule. By a rise in pressure, a normal explosion can develop from the "cold flames." By introducing hydrocarbon-air mixtures under pressure into heated reaction chambers, very peculiar explosion limits are observed as a function of the pressure and the temperature (*cf.* Sec. C). In a certain pressure range, there are three ignition limits. With rising temperature, ignition is obtained which is absent at higher temperatures and which is again obtained only at still higher temperatures. These phenomena are certainly determined by the same conversions that cause the appearance of cold flames. Since no anomalies have been observed in ignition by adiabatic compression of hydrocarbon-air mixtures, as far as measurements are available, those phenomena as well as the cold flames could partly be caused by wall effects.

<sup>1</sup> By this term, we shall understand, as the meaning of the word suggests, the differential quotient of the reaction velocity with respect to the temperature, which can be positive or negative. Frequently it is used to mean the factor by which the reaction velocity changes, with a rise in temperature, by 10°. This factor can be  $\geq 1$ , but it is always  $> 0$ .

Hydrocarbon oxidation is at any rate a chain reaction (with branching), as can be concluded, among other things, from the generally possible inhibition by the wall and by packing of the reaction chamber, as well as from the sensitivity to additions. A number of important observations on the oxidation behavior of hydrocarbons have been derived from experiences on engine combustion (*cf.* Chap. XII) and can readily be fitted in the framework of the other findings.

In the investigation of the individual hydrocarbons, the partial phenomena discussed in the foregoing are often found simultaneously in the most confusing manner, often by various authors in apparent contradiction to one another. The individual factors, such as the participation of impurities or of products produced in the reaction and the influence of the various conditions of the wall (in simple cases, *cf.* pages 430ff., 433), yield such a welter of combinations that we are not surprised at the appearance of even apparently contradictory phenomena. This situation excludes the possibility of arranging the results of all authors in a unified complete scheme, however, since this would not be possible without disregarding many important and certainly sound individual observations. The reader who does not wish to lose himself in the mass of experimental detail may skip to the theoretical treatment of the processes (Sec. D), in which an attempt is made to furnish a complete picture of the phenomena, the personal opinions of the author remaining, of course, in the background. For a more complete understanding, it will also be necessary to become familiar with the individual observations.

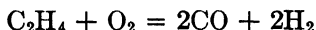
#### A. COMBUSTION OF HYDROCARBONS IN THE FLAME

Conclusions respecting the explosive combustion of hydrocarbons can be derived from: (1) flame velocities, (2) spectroscopic finding, and (3) the analysis of the end products obtained in an explosion. These observations alone do not suffice for a clarification of the reaction mechanism, but they are nevertheless interesting and suggest certain conclusions. If we allow hydrocarbons to burn with a quantity of air or oxygen not sufficient for the complete oxidization into  $\text{CO}_2 + \text{H}_2\text{O}$ , we obtain  $\text{CO}$ ,  $\text{H}_2\text{O}$  and  $\text{CO}_2$  and  $\text{H}_2$  as reaction products in relation to one another in the ratio of the constants<sup>1</sup> of the water-gas equilibrium, for the temperature at which equilibrium can appear. If the air quantity is further reduced, carbon in the form of soot also appears and is responsible for the illumination of nonpremixed gas flames. Experiments are not lacking to set up general rules regarding the primary action of oxygen in combustion; theories have been advanced for favored hydrogen

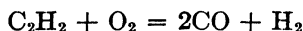
<sup>1</sup> Numerical values can be found in E. Justi (cited p. 226); in the cooling of the gas mixture, the equilibrium "freezes" because the reaction velocity becomes too small. The freezing temperature depends on the cooling velocity.

combustion or carbon combustion, but they do not do justice to the actual findings.

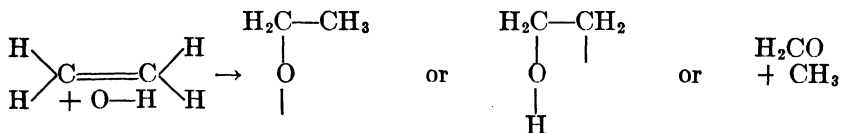
**1. Reaction Products in Explosion and Combustion.**—Dalton, for example, has observed, and Bone<sup>1</sup> has rediscovered, that, in the explosion of ethylene with an equal volume of oxygen, no soot is given off but rather that the conversion takes place according to



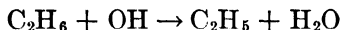
The explosion of acetylene follows an analogous course:



If, for example, OH (in small concentration) should be a product participating in the combustion, to which many observations attest (*cf.* page 325), it would have to react with these compounds in such a manner that O would act on the carbon but not on the hydrogen, as, for instance,



That something similar occurs is not improbable, but it is of course not proved. In acetylene, we can naturally imagine the same thing but not in ethane where a double bond is no longer present. If OH were to react with ethane, the following reaction would come into consideration as the most likely one:



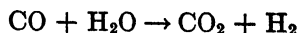
Since in this manner a part reacts into H<sub>2</sub>O, there is no longer enough oxygen for the combustion of the total C, and we should therefore necessarily obtain soot in the explosion of ethane, assuming the same volume of oxygen. This is actually the case. It was found, for example, that the combustion gas consists of 4.2 per cent CO<sub>2</sub>, 33.5 per cent CO, 2.7 per cent hydrocarbons, 11 per cent methane, and 48.6 per cent hydrogen; in addition, water is condensed out, and one-sixth of the original carbon is given off as soot. Because of the reaction  $\text{C} + \text{H}_2\text{O} = \text{CO} + \text{H}_2$ , the composition of the end products depends greatly on external factors that influence the flame temperature.

Methane reacts with the same volume of oxygen according to



<sup>1</sup> *Cf.* the presentation in the Bakerian lecture by W.A. Bone, *Proc. Roy. Soc. London*, A, **137**, 243 (1932). BONE, W.A., and B. LEAN, *J. Chem. Soc.*, **61**, 873 (1892). BONE and TOWNEND, "Flame and Combustion in Gases." BONE, W.A., and J.C. CHAIN, *Trans. Chem. Soc.*, **71**, 26 (1897).

to which is added<sup>1</sup> the water-gas reaction



For further observations of this kind, we refer to Bone.

Bone attempts to present the course of combustion as a result of hydroxylation and splitting. In this manner, a list of the possible reaction products of the combustion is obtained, to be sure, but the actual course of reaction is by no means reproduced.

Of further interest are experiments that determine the relative combustibility of  $\text{H}_2$ ,  $\text{CO}$ , and hydrocarbons.<sup>2</sup> Here certain conceptions of the relative velocity prevailed, which we sometimes meet occasionally even now and for which there is no actual experimental support. Bone and his associates exploded the following mixtures:  $\text{C}_2\text{H}_6 + \text{O}_2$ ,  $\text{C}_2\text{H}_4 + \text{H}_2 + \text{O}_2$ , and  $\text{C}_2\text{H}_2 + 2\text{H}_2 + \text{O}_2$ , that is, three mixtures of the same gross composition. Although considerable soot production is obtained in ethane, as was discussed above, the two other mixtures yielded no soot, not even in the presence of added hydrogen. The hydrogen, therefore, is not favored in combustion. In analogous experiments with methane, it was shown that, in the explosion of  $\text{CH}_4 + \text{O}_2 + 2\text{H}_2$ , about 95 to 97 per cent of the methane present is consumed. A similar result was obtained when the hydrogen was replaced by  $\text{CO}$ ; here, too, no carbon was formed.<sup>3</sup>

**2. Spectroscopic Observations. Reaction of Free Atoms and Radicals.**—The flames of hydrocarbons show, as has already been discussed (page 231), the bands of  $\text{C}_2$ ,  $\text{CH}$ , and  $\text{OH}$  and in addition more or less intensely the Vaidya bands in the ultraviolet, which are probably to be attributed to  $\text{HCO}$ . It is quite probable, from the analogous findings of Kondratjew in the case of  $\text{CO}$  and  $\text{H}_2$  combustion, that, of these radicals,  $\text{OH}$  plays an essential role in combustion; but up to the present this has not been directly proved. In the case of the other radicals, we naturally also suspect a participation in the reaction, but no direct experiments have been made on this participation. In addition to these radicals, we may with certainty assume the presence of hydrogen atoms and perhaps also suspect a participation in the reaction. Perhaps oxygen atoms, whose concentration will always remain smaller than that of  $\text{H}$ -atoms, likewise participate. In addition, under certain circumstances,  $\text{HO}_2$ -radicals perhaps take part, the formation of which from  $\text{H}$  and  $\text{O}_2$  is to be assumed in hydrogen-oxygen combustion (page 317).

<sup>1</sup> In cooling, the water-gas equilibrium commonly "freezes."

<sup>2</sup> Cf. BONE, "Flame," quoted p. 156.

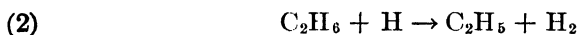
<sup>3</sup> The composition of the explosion products is dependent on the presence of inactive gases which, insofar as they do not interfere in the reaction as triple-collision partners, simply effect a lowering of the temperature. Cf. BONE, W.A., and L.E. AUTTRIDGE, *Proc. Roy. Soc. London, A*, **157**, 234 (1936).

In the action of H-atoms produced in the discharge (Bonhoeffer and Harteck)<sup>1</sup> or O-atoms (Hartek<sup>2</sup> and Kopsch) on hydrocarbons, the same spectra appear as in hydrocarbon combustion (in the former case, naturally, with the exception of the OH bands), which at least does not make it appear unlikely that analogous reactions take place also in combustion.

The reaction of H-atoms with hydrocarbons was first investigated by Bonhoeffer and Harteck<sup>1</sup> and was the object of many later investigations.<sup>3</sup> All the hydrocarbons investigated, with the exception of methane, already react with H-atoms at low temperatures. According to Geib and Harteck,<sup>3</sup> it cannot be proved that even at 183°C H-atoms react in the sense of the equation  $\text{H} + \text{CH}_4 = \text{CH}_3 + \text{H}_2$ , from which an activation heat of at least 15 kcal can be concluded. This activation heat is low enough, however to attribute a considerable role to this reaction in flames. The reaction  $\text{CH}_3 + \text{H}_2 = \text{CH}_4 + \text{H}$  demands an activation energy of about  $9 \pm 2$  kcal.<sup>4</sup> Ethane is easily acted upon by atomic oxygen, yielding methane in considerable quantities as a reaction product. In this, the reaction



which takes place with an activation energy of  $\sim 7$  kcal, as well as



with an activation energy of  $\sim 9$  kcal, probably play a role.<sup>5</sup> (1) is said to take place about about four times more rapidly than (2).<sup>6</sup> In

<sup>1</sup> BONHOEFFER, K.F., and P. HARTECK, *Z. physik. Chem.*, Sec. A, **139**, 64 (1928).

<sup>2</sup> HARTECK, P., and U. KOPSCH, *Z. physik. Chem.*, Sec. B, **12**, 327 (1931).

<sup>3</sup> GEIB, K.H., and P. HARTECK, *Z. physik. Chem.*, Sec. A, **170**, 1 (1934). GEIB, K.H., and E.W.R. STEACIE, *Z. physik. Chem.*, Sec. B, **29**, 215 (1935). Cf. particularly GEIB, K.H., *Ergeb. exakt. Naturw.*, **15**, 44 (1935). Habil. schr., Leipzig, 1937. TAYLOR, H.S., and D.A. HILL, *Z. physik. Chem.*, Sec. B, **2**, 449 (1929). v. WARTENBERG, H., and G. SCHULTZE, *Z. physik. Chem.*, Sec. B, **2**, 1 (1929). Cf. also the collective review by L. v. Müffling, and R. Macs, *Z. Elektrochem.*, **44**, 428 (1938). Further, MORIKAWA, K., W.S. BENEDIKT, and H.S. TAYLOR, *J. Chem. Phys.*, **5**, 212 (1937). STEACIE, E.W.R., *J. Chem. Phys.*, **6**, 37 (1938). STEACIE, E.W.R., and N.W.F. PHILLIPPS, *J. Chem. Phys.*, **4**, 461 (1936); **5**, 275 (1937). TRENNER, N.R., K. MORIKAWA, and H.S. TAYLOR, *J. Chem. Phys.*, **5**, 203 (1937).

<sup>4</sup> v. HARTEL, and M. POLANYI, *Z. physik. Chem.*, Sec. B, **11**, 97 (1931). v. BOGDANDY, and M. POLANYI, *Z. Elektrochem.*, **33**, 554 (1927). H.S. Taylor and Rosenblum [*J. Chem. Phys.*, **6**, 119 (1938)] give about 11 kcal.

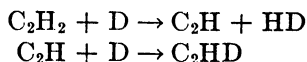
This value of the activation heat is given by J.P. Cunningham and H.S. Taylor [*J. Chem. Phys.*, **6**, 359 (1938)].

<sup>5</sup> HARTECK, P., *Trans. Faraday Soc.*, **30**, 134 (1934).

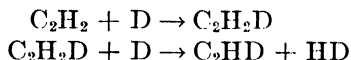
<sup>6</sup> STEACIE, E.W.R., and PHILLIPPS, *Can. J. Research*, **16**, Sec. B, 303 (1938).

addition to methane, ethylene and acetylene are produced in small quantities. Analogous reactions probably occur in the higher hydrocarbons.<sup>1</sup>

Hydrogen has a hydrating effect on ethylene; in addition, small quantities of acetylene are produced, while acetylene is hydrated to only a very slight degree. It catalyzes the recombinations of the H-atoms a great deal, however. An exchange with deuterium atoms also takes place, a sign that a lively reaction occurs but that it does not lead to hydration. Geib and Steacie therefore assume the following reactions (with D-atoms; the same conversions naturally appear with H-atoms, but it is not so easy to prove they are present):

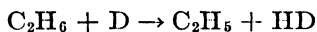


or also, by reversing the order of hydration and dehydration,



Pentane is reduced into lower fractions by atomic hydrogen, principally propane, in addition to  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ , and  $\text{CH}_4$ . These reactions are probably typical for paraffins. In addition to hydration, benzol likewise experiences a disintegration into  $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ , and small quantities of  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_6$ .

Our knowledge of that kind of reaction has been greatly advanced by the discovery of the heavy hydrogen isotope, deuterium; because, with it, the presence of conversions that persist in an exchange of H-atoms may be proved analytically.<sup>2</sup> Ethane might also react with D-atoms according to



with an activation energy of about 11 kcal. The activation heats thus computed are not very accurate; but, since we are especially interested in the reactions in the flame where all reactions with activation heats of this order of magnitude take place extremely rapidly, a more accurate knowledge is not necessary. It is therefore certain that, under such conditions, hydrocarbons are rapidly disintegrated by H-atoms. It is not unlikely that analogous reactions would likewise take place with OH-radicals. Up to the present, direct investigations are lacking.

<sup>1</sup> For the reaction of the hydrocarbons in general and the reaction of H-atoms in particular, see the lectures of the Faraday meeting in April, 1939 (*Trans. Faraday Soc.*, August, 1939). According to Steacie (see the lectures) the above reaction (1), which was not very probable, can be omitted. In its place, reactions like  $\text{C}_2\text{H}_5 + \text{H} \rightarrow 2\text{CH}_3$  are to be assumed at high H-atom concentration, and analogous reactions in the case of radicals with greater numbers of C-atoms.

<sup>2</sup> Cf. also the abstract by K.H. Geib, *Z. Elektrochem.*, **44**, 81 (1938).

On the other hand, something is known about the reactions of the oxygen atoms,<sup>1</sup> and this knowledge derives from investigations on the effect on organic matter of O-atoms pumped from a gas discharge. The succession of the ability to react of paraffins toward O-atoms is the same as toward H-atoms. Methane is acted upon most powerfully. In pentane and hexane, the activation energy amounts to only about 5 kcal. In benzol and acetylene, it is under 4 kcal. Attention has already been called to the chemiluminescence in these reactions. In the effect on pentane, the bands of OH and CH were observed; in benzol and acetylene, those of CC were also observed. As reaction products, H<sub>2</sub>O, CO, CO<sub>2</sub>, and H<sub>2</sub> were found. Since the velocity of the oxidation of CO by atomic oxygen under the experimental conditions is known, however, it can be concluded from the fact that CO and CO<sub>2</sub> frequently appear in about the same amounts that only about 5 per cent of the CO formed can have gone over into CO<sub>2</sub> by direct oxidation with oxygen atoms and that therefore the main part of the CO<sub>2</sub> must have been produced in a different manner, either by the disintegration of the intermediary products, *e.g.*, HCOOH, or by the effect of OH on CO. It follows, at any rate, since these investigations have been carried out at room temperature and partly at the temperature of liquid air, that hydrocarbons are rapidly disintegrated by oxygen atoms under flame conditions.

If assigning the Vaidya bands to the radical HCO should prove to be correct, it would follow that perhaps this radical also plays a role in the flame. The formation of an HCO-radical must be assumed in the effect of atomic hydrogen on CO in which formaldehyde and glyoxal are obtained as stable reaction products.<sup>2</sup> According to this, it must be assumed that HCO is produced in only a fraction of the triple collisions of H and CO (about every five thousandth triple collision) and that it easily disintegrates spontaneously again.<sup>3</sup> It can then react in a triple collision with atomic hydrogen to form formaldehyde, insofar as no H<sub>2</sub> + CO forms instead. In addition, 2 HCO in triple collision can either form glyoxal or furnish formaldehyde and CO.

<sup>1</sup> Cf. GEIB, K.H., cited p. 315. HARTECK, P., and U. KOPSCH, *Z. physik. Chem.*, Sec. B, **12**, 327 (1931). GEIB, K.H., and P. HARTECK, *Ber. deut. chem. Ges.*, **66**, 1815 (1933); *Trans. Faraday Soc.*, **30**, 131 (1934).

<sup>2</sup> Cf. GEIB, K.H., cited p. 315. FRANKENBURGER, W., *Z. Elektrochem.*, **36**, 757 (1930). FARKAS, L., F. HABER, and P. HARTECK, *Naturwissenschaften*, **18**, 266 (1930). FARKAS, L., and P. HARTECK, *Naturwissenschaften*, **18**, 433 (1930). FARKAS, L., and H. SACHSSE, *Z. physik. Chem.*, Sec. B, **27**, 111 (1934).

<sup>3</sup> According to experiments by E. Gorin [*Acta Physicochim. URSS*, **8**, 513 (1938)] and independent computations by C.E.H. Bawn [*Trans. Faraday Soc.*, **34**, 598 (1938)], an activation energy of  $\sim 16$  to 20 kcal is necessary for HCO disintegration, and this would indicate a considerable life span of HCO. Further experiments will have to be made on this reaction. Cf. also GORIN, E., *J. Chem. Phys.*, **7**, 256 (1939).

All reactions that take place with detectable velocity at low temperatures proceed with certainty at high temperatures. Insofar as there are no other still more rapid reactions, they must play a role in the total reaction in the flame.

**3. Flame Velocities.**—Observations on flame velocities permit several further conclusions. The results of an investigation by Bone, Fraser, and Lake<sup>1</sup> on the influence of acetylene on the flame velocity in an oxygen-hydrogen mixture are remarkable, for example. The addition of only 1 per cent of acetylene lowers the flame velocity by about 50 per cent, whereas more acetylene raises it again. With 10 per cent of acetylene, there is a maximum of the velocity with a value that is twice as high as the flame velocity of a pure oxygen-hydrogen mixture. Particularly the influence of the small amount of acetylene might be explained solely by the reaction velocity. It is reasonable to assume that H-atoms (and perhaps other active particles) that play a role in oxygen-hydrogen combustion and flame propagation are destroyed by the influence of the acetylene (*cf.* page 373).

The normal combustion velocity of carbon monoxide is accelerated by small quantities of almost all organic materials investigated. Since it is known (*cf.* Chap. III, page 121) that the flame velocity of CO and the velocity of its slow oxidation are greatly increased by small amounts of H<sub>2</sub> and H<sub>2</sub>O, the influence of organic substances can simply be attributed to the H<sub>2</sub> split off from these or to the H<sub>2</sub>O produced by combustion. It is quite conceivable that an especially high concentration of radicals (*e.g.*, of OH) prevails as the result of hydrocarbon combustion and that this is responsible for the acceleration of the combustion velocity of the CO. Information on this point, however, can be gained only by special experiments to determine these radical concentrations under various conditions (*cf.* the investigations by Kondratjew on H<sub>2</sub> and CO oxidation, pages 323, 339). For the influence on the combustion velocity of CO by organic substances, *cf.* especially Hartmann.<sup>2</sup>

The normal combustion velocity of hydrocarbons in mixture with air or oxygen always reaches its maximum for mixtures with a certain fuel excess. Parallel with this is the fact that the velocity of slow oxidation also generally reaches its maximum decidedly on the side of fuel excess (*i.e.*, the reaction in respect to the fuel is of essentially a higher order than corresponds to the stoichiometric equation). It is reasonable to assume that the conditions in the flame likewise reflect the influence of the reaction velocity, even though this is not proved as yet. The other possible explanation would be that in fuel excess the

<sup>1</sup> BONE, W.A., R.P. FRASER, and F. LAKE, *Proc. Roy. Soc. London, A*, **131**, 1 (1931).

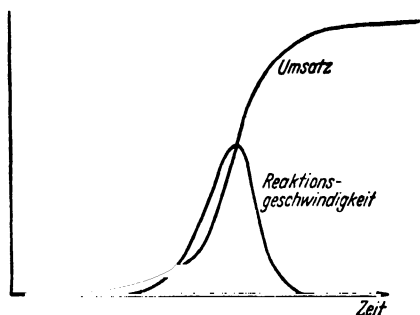
<sup>2</sup> HARTMANN, E., Dissertation at Karlsruhe, 1931, "Der Verbrennungsmechanismus des Kohlenoxyds und seiner Gemische mit Gasen und Dämpfen."



possibility of the liberation of hydrogen and the formation of free hydrogen atoms is probably greater than with a lack of fuel. Since on the other hand H-atoms diffuse especially rapidly and thus help to propagate the combustion, an acceleration of the combustion velocity would therefore result from fuel excess. This factor and that of the reaction velocity need not necessarily be independent of one another, since in both cases the influence of the H-atoms is decisive. An explanation would be possible only by a systematic analysis of the flame velocities—both experimental and theoretical.

## B. THE SLOW OXIDATION OF HYDROCARBONS

**1. General Remarks.**—If hydrocarbons in mixture with air or oxygen at pressures that can range from 1 to several atm are raised to a moderately high temperature in a container, say, 200° to 300° or perhaps above



(Umsatz = conversion  
Reaktionsgeschwindigkeit = reaction velocity)  
Zeit = time

FIG. 186.—Variation of conversion and reaction velocity with the time in hydrocarbon oxidation, schematic.

the temperature must be higher in paraffins, for example, the shorter the hydrocarbon chain of the molecule; in ethane, temperatures in the neighborhood of ~ 300°C suffice), then the following is noted: At first, there is an “induction period,” which can vary between seconds and hours depending on the experimental conditions and during which apparently nothing happens, at least insofar as the analysis is not extended to small traces. After that, of course without a sharp transition, the reaction begins noticeably and is accelerated. Finally, when a considerable portion has been reacted, it slowly dies down. Figure 186 gives the course of conversion and reaction velocity in time. Thus we obtain the typical course of an “auto-catalytic” reaction, *i.e.*, a reaction whose velocity is increased by a product produced in the conversion itself until it finally dies down as the result of the destruction of the initial materials. Such a course of reaction differentiates itself from an explosion only by the fact that it does not lead to a disturbance of the heat equilibrium and thus to a rise in temperature. Experimentally the process can be studied in various ways. The mixture can be put into a heated, closed reaction chamber and the conversion observed (a) by noting the pressure change during the reaction or (b) by an analysis of the reaction gas taken out at a certain time. Obviously, observing the reaction from the change in pressure alone is not very satisfactory,

especially since the latter differs according to whether the combustion yields primarily CO or CO<sub>2</sub>, which can be quite different for different stages of the reaction. In observing the reaction, it is simple to determine the consumption of oxygen, the CO and CO<sub>2</sub> formed, and also water; but it is more difficult to establish quantitatively other reaction products and intermediary products of an organic nature; and it is especially difficult, particularly in the higher hydrocarbons, to determine the consumption of the initial materials, which are, of course, of special interest. The information that various investigations yield on the course of the reaction is therefore to be judged quite differently according to the method of analysis employed. Determining the change in pressure

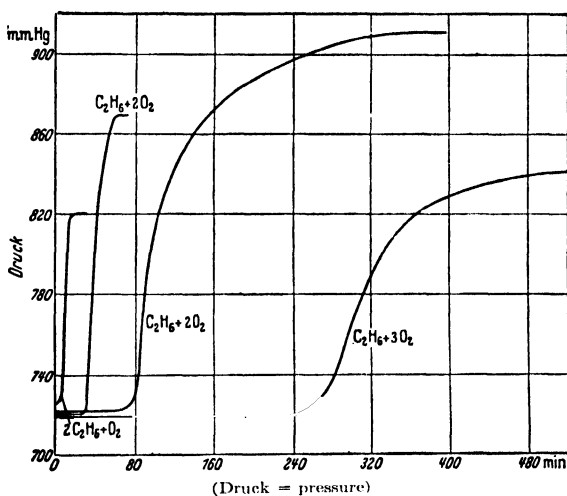


FIG. 187.—Oxidation of various ethane-oxygen mixtures, change in pressure as the measure of conversion. [From Bone and Hill, *Proc. Roy. Soc. London, A*, vol. 129 (1930).]

alone yields the fewest conclusions on the course of the reaction. Many experiments have been carried out with flowing gases, the mixture being led through a heated reaction tube and the escaping gases analyzed. Generally flow experiments are made at atmospheric pressure so that fewer variations are present than in static experiments in which the pressure too is varied. However, it is possible to work at increased or decreased pressure in flowing systems too, and such experiments have been made especially for higher pressures.<sup>1</sup>

The velocity of the oxidation of hydrocarbons can depend to a great degree on the condition of the chamber wall, as will be shown later in individual examples. In Fig. 187 from Bone and Hill, we present a typical course of the conversion in time as it has again and again been

<sup>1</sup> For example, by S.P. Burke, C.F. Fryling, and T.E.W. Schumann [*Ind. Eng. Chem.*, **24**, 804 (1932)] at pressures up to over 100 atm.

observed in hydrocarbon oxidation. It concerns the oxidation of ethane measured by pressure changes. The induction times vary here, at constant initial pressure, from about 3 min to about 4 hr, depending on the composition of the mixture. The mixture richest in ethane is most capable of reaction.

As intermediary products of the oxidation, aldehyde, and particularly formaldehyde, acids, and, in addition, all kinds of other products are obtained. Alcohols do not appear to belong to the normal intermediary products, but they can be obtained in considerable concentrations under certain circumstances.<sup>1</sup> The role played in the course of the reaction by peroxide-like materials that could be demonstrated in small concentration will be discussed later. A phenomenon connected with hydrocarbon oxidation that can be observed in the most varied materials is the appearance of a luminescence and the so-called "cold flames" which were first observed by Perkin<sup>2</sup> in the case of ether vapors in air and which have recently been investigated frequently and in detail (see pages 437ff.).<sup>3</sup>

**2. The Kinetics of the Oxidation of Lower Aldehydes.**—Aldehydes appear as intermediary products in the oxidation of all hydrocarbons and probably play an important role in their oxidation. We shall therefore treat first what is known about the slow combustion of aldehydes.<sup>4</sup>

*a. Formaldehyde.*—Askey<sup>5</sup> investigated the reaction of  $\text{H}_2\text{CO} + \text{O}_2$  between 320° and 400°. The reaction takes place by way of chains, since it is suppressed by the packing of the reaction chamber.

Fort and Hinshelwood<sup>6</sup> find temperatures for (150 mm  $\text{CH}_4 + 300$  mm  $\text{O}_2$ ), (100 mm  $\text{CH}_3\text{OH} + 200$  mm  $\text{O}_2$ ), and (200 mm  $\text{HCHO} + 200$  mm  $\text{O}_2$ ), for which the half-life period for the conversion amounts to 5 min, or 470°, 442°, and 321°, respectively, as well as an apparent activation energy of 61.5, 62.5, and 20.6 kcal, respectively. The reaction is inhibited by packing; i.e., the formaldehyde oxidation

<sup>1</sup> D.M. Newitt and J.B. Gardner [*Proc. Roy. Soc. London, A*, **154**, 329 (1936)] observed alcohol formation in the slow oxidation of methane and ethane also at atmospheric pressure. For methane, they obtained 0.3 to 0.7 per cent of the burned gas as methanol. The ratio of methanol to aldehyde was between 0.08 to 0.21; in ethane, somewhat higher yields of ethanol and methanol were obtained. For propane oxidation, see p. 433.

<sup>2</sup> PERKIN, W.H., *J. Chem. Soc.*, **44**, 363 (1882).

<sup>3</sup> WHITE, A.G., *J. Chem. Soc.*, **121**, 2561 (1922). EMELEUS, H.J., *J. Chem. Soc.*, 1926, p. 2948; 1929, p. 1733. PRETTE, M. Cf. the summary, L'inflammation et la combustion explosive en milieu gazeux, II, Les hydrocarbonés, *Act. sci. et ind.*, No. 105, Paris, 1934.

<sup>4</sup> No induction period is noted in the oxidation of aldehydes at higher temperatures. Since, in addition, aldehydes are able to reduce the induction period otherwise appearing in hydrocarbon oxidation, it is at least not improbable that the decisive reaction during the induction period of the slow hydrocarbon oxidation is the formation of aldehydes, probably at the wall.

<sup>5</sup> ASKEY, J., *J. Am. Chem. Soc.*, **52**, 974 (1930).

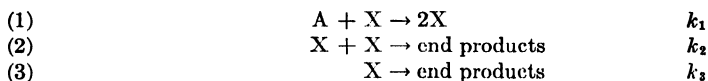
<sup>6</sup> FORT, R., and C.N. HINSHELWOOD, *Proc. Roy. Soc. London, A*, **129**, 284 (1930).

becomes noticeable in the neighborhood of 300°. The lower apparent activation heat suggests that wall processes play a considerable role in formaldehyde oxidation.

More recent investigations have been made by Bone,<sup>1</sup> Spence,<sup>2</sup> and Style.<sup>3</sup> Snowdon and Style have carefully investigated the reaction in the neighborhood of 300°C partly by gas analysis and partly by determining the formaldehyde concentration by the optical method.<sup>4</sup> The experiments were made in a quartz container and were, as has been observed again and again, reproducible only if several experiments had been made in the container. Snowdon and Style can state their experiments (as well as those of Spence) by an expression

$$(I) \quad -\frac{d[A]}{dt} = k[A] \cdot [A] - C\}$$

in which A is the aldehyde and  $k$  and  $C$  are constants that can still depend considerably on the condition of the wall, especially  $C$ . The expression (I) can be derived from a mechanism that is similar to the one by Bodenstein to be discussed below (page 382).



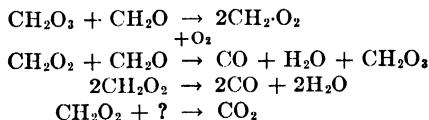
Thus two chain-breaking reactions (2) and (3) of the second and first order are assumed, of which the latter probably takes place at the wall. The active substance appearing in it and in the chain-branching reaction (1) is probably of a peroxide nature (cf. pages 381ff. below). The scheme above leads to the expression

$$(II) \quad -\frac{d[A]}{dt} = \frac{k_1^2}{k_2} [A] \left\{ [A] - \frac{k_3}{2k_1} \right\}$$

A comparison of (I) and (II) shows the meaning of the empirical constants  $k$  and  $C$ . Numerical values {if the time is measured in minutes and the partial pressure for  $[A]$  is given in mm Hg} in an experiment at 344°C were  $k = 1.42 \cdot 10^{-3}$  and  $C = 29$ .

CO, CO<sub>2</sub>, H<sub>2</sub>O, and perhaps H<sub>2</sub>, formic acid, and peroxide in very small quantities appear as reaction products. Intentional addition of CO inhibited the reaction somewhat and led to increased CO<sub>2</sub> formation;  $k$  and  $C$  change with the temperature, corresponding to apparent activation energies of 25 and -12 kcal. The opposite course of the temperature is to be employed in the form of (II).

It is also possible to interpret the quantities of CO<sub>2</sub> formed in the reaction by the basic velocity expression if the latter is specialized in the following manner by the introduction of the peroxidic active materials CH<sub>2</sub>O<sub>2</sub> and CH<sub>2</sub>O<sub>3</sub> assumed by Spence:



This scheme again leads to (I) but represents only a preliminary attempt. It is assumed that the active materials X are formed primarily at the wall and that in  $k$  there is present a further wall influence that is not yet clear.

<sup>1</sup> BONE and GARDNER, *Proc. Roy. Soc. London, A*, **154**, 297 (1936).

<sup>2</sup> SPENCE, *J. Am. Chem. Soc.*, **58**, 649 (1936).

<sup>3</sup> SNOWDON, F.F., and D.W.G. STYLE, *Trans. Faraday Soc.*, **35**, 426 (1939).

<sup>4</sup> SLOTIN, L., and D.W.G. STYLE, *Trans. Faraday Soc.*, **35**, 420 (1939).

Various treatments of the wall greatly influenced the reaction velocity. Treatment by hydrofluoric acid had an extremely inhibiting effect, whereas treatment with Hg had a greatly accelerating effect.

Formaldehyde oxidation has also been investigated under the influence of light.<sup>1</sup> The reaction can be interpreted as oxidation of the aldehyde into formic acid with subsequent partial disintegration of the acid into  $\text{CO} + \text{H}_2\text{O}$  and in a lesser degree  $\text{CO}_2 + \text{H}_2$ . On the mechanism of the reaction, little can be said. The quantum yield is in the neighborhood of 10 at  $100^\circ\text{C}$ , which would indicate a chain reaction, even though the photochemical disintegration of the formaldehyde<sup>2</sup> with a quantum yield of 1 probably does not take place by way of chains. Lewis and v. Elbe (cited page 386) discuss a mechanism for the reaction which takes stimulated formaldehyde molecules as its point of departure.

*b. Acetaldehyde.*—The slow oxidation of acetaldehyde has, up to the present, been investigated most thoroughly, the first work being done by Bodenstein<sup>3</sup> and his associates. The reaction can be observed at low temperatures, below  $100^\circ\text{C}$ , from about  $60^\circ$  on. Peracetic acid  $\text{CH}_3\text{C}(\text{CO})\cdot\text{OOH}$  appears as the chief reaction product at these temperatures. At higher temperatures, we should of course obtain disintegration products of this acid.

The oxidation of aldehydes can also be observed at low temperatures in the liquid phase and has been investigated very carefully. In this connection, the phenomenon of "negative catalysis" is observed; *i.e.*, some materials added in small quantities (*e.g.*, diphenylamine) can greatly inhibit the oxidation. The most natural explanation is that we are here dealing with a chain reaction with relatively long chains that can be broken off by the added substance.<sup>4</sup> That this explanation is correct has been directly verified experimentally by Bäckström by having the same reaction (oxidation of benzaldehyde) take place in the dark and in light. The ratio of the number of converted molecules to absorbed quanta yields the extent of the reaction chain.

In the aldehyde oxidation in solution, we are dealing with a typical "auto-oxidation process." By this, the following is meant:<sup>5</sup> A substance

<sup>1</sup> PATAT, F., *Z. physik. Chem., Sec. B*, **25**, 208 (1934); *Z. physik. Chem., Sec. B*, **27**, 431 (1934). NORRISH, R.G.W., and KIRKBRIDE, *J. Chem. Soc.*, 1932, p. 1518. CARRUTHERS and NORRISH, *Trans. Faraday Soc.*, **32**, 195 (1936); *J. Chem. Soc.*, 1936, p. 1036. Cf. also GORIN, E., *J. Chem. Phys.*, **7**, 256 (1939).

<sup>2</sup> Quoted p. 380.

<sup>3</sup> BODENSTEIN, M., *Z. physik. Chem., Sec. B*, **12**, 151 (1931); *Sitzber. preuss. Akad. Wiss. physik. math. Klasse*, 1931, p. 73.

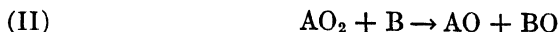
<sup>4</sup> CHRISTIANSEN, J.A., *J. Phys. Chem.*, **28**, 145 (1924). BÄCKSTRÖM, *J. Am. Chem. Soc.*, **49**, 1460 (1927). BÄCKSTRÖM and H. ALYEA, *J. Am. Chem. Soc.*, **51**, 90 (1929). BÄCKSTRÖM, *Z. physik. Chem., Sec. B*, **25**, 99 (1934). Cf. also SEMENOFF, N., "Chemical Kinetics and Chain Reactions." BÄCKSTRÖM and BEATTY, *J. Phys. Chem.*, **35**, 2530 (1931). BÄCKSTRÖM, *Trans. Faraday Soc.*, **24**, 601 (1928).

<sup>5</sup> ENGLER, C., and J. WEISSBERG, "Vorgänge der Autoxydation," Brunswick, 1904. ENGLER and WILD, *Verh. naturwiss. Ver. Karlsruhe*, **13**, 71; **20**, 11 (1896);

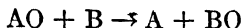
A forms an intermediate peroxide with oxygen



The peroxide, the auto-oxidizer, oxidizes a molecule of the "acceptor" B, while it is reduced itself



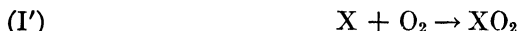
eventually followed by



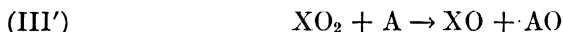
If no particular acceptor B is present, the following reaction can take its place:



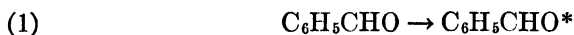
According to Semenov (cited page 404), a somewhat more general form of the auto-oxidation theory is obtained<sup>1</sup> if it is assumed that not necessarily an initial substance readily accepts  $O_2$ , but that an intermediate or terminal product of reaction, perhaps X, can come into consideration just as well and react to form a peroxide



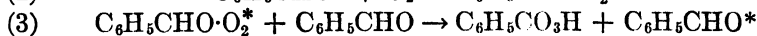
-which then oxidizes a molecule of the initial material according to



For the oxidation of benzaldehyde, Bäckström and Beatty (cited page 380) suggest the following reaction mechanism:



in which  $C_6H_5CHO^*$  is to represent a stimulated molecule



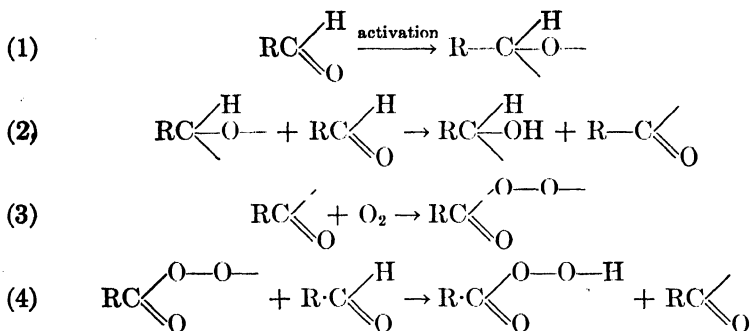
in which  $C_6H_5CO_3H$  is the oxidation product, perbenzoic acid. In this, the essential fact is not that the individual compounds given above appear (a stimulated molecule that differs from the normal only by its energy content generally has a very short life and is not very likely as an intermediate product, since it does not differ from the normal in its chemical constitution); it is solely important that a corresponding succession of

*Ber. deut. chem. Ges.*, **30**, 1669 (1897). BACH, *Compt. rend.*, **124**, 951 (1897). STAUDINGER, H., *Ber. deut. chem. Ges.*, **53**, 1075 (1925). MOUREU, C., *Trans. Faraday Soc.*, **24**, 707 (1928).

<sup>1</sup> This conception was also essentially presented by Engler by his assumption of "indirect auto-oxidizers."

reaction phases takes place—an activated product formed from the aldehyde which is able to attach an oxygen molecule, and an initial molecule oxidized with regeneration of the activated compound. It can be shown directly by experiment<sup>1</sup> that benzaldehyde during its oxidation exercises a much stronger oxidizing effect on added foreign substances than the perbenzoic acid. Hence an intermediate product of especially high oxidation power must have been formed.

For the oxidation of liquid aldehyde, Bäckström<sup>2</sup> later suggested the following series of reactions:



The really activated substance here is therefore a radical  $\text{R}-\text{C} \begin{array}{c} \text{H} \\ \diagup \\ \text{O} \end{array}$  (cf. Ubbelohde<sup>3</sup>).

Even though details of this scheme will probably have to be modified, the characteristic features will remain and the results of the solutions suggest certain conclusions for the reaction in the gas phase.

For the oxidation of acetaldehyde in the gas phase between 50° and 90°, Bodenstein (cited page 380) found the following velocity expression:

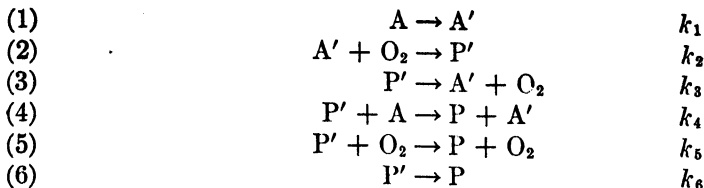
$$\frac{d[\text{P}]}{dt} = \frac{k_1 k_4 [\text{A}]^2}{k_5 [\text{O}_2] + k_6} \quad (1)$$

in which P is the peracetic acid formed and A the aldehyde. The signs for the constants correspond to the reaction scheme by Bodenstein, which is given below. To derive this reaction scheme, Bodenstein assumed the following reactions:

<sup>1</sup> According to Semenoff (cited p. 404), Bach and Engler had already noted this, and this observation has been substantiated by recent investigations by Jorissen and van der Bèck [*Rec. trav. chim.*, **49**, 138 (1930)].

<sup>2</sup> BÄCKSTRÖM, H.L.J., *Z. physik. Chem.*, Sec. B, **25**, 99 (1934).

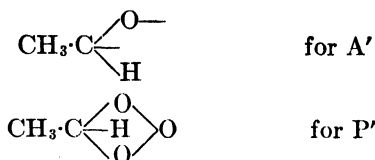
<sup>3</sup> UBBELOHDE, A.R., "The Science of Petroleum," Vol. IV, pp. 2937ff., Oxford, 1938.



The symbols are as follows:

A acetaldehyde; A' an activated molecule produced by it; P' an intermediary product rich in oxygen; P peracetic acid.

Specifically it can be assumed



In regard to this scheme, it should be noted that, for one thing, it adapts itself to the more general form of the auto-oxidation reaction according to Semenov (which was suggested later than this scheme by Bodenstein) and that, for another thing, it has much in common with Bäckström's scheme for aldehyde oxidation (likewise suggested later. The apparent activation energy of aldehyde oxidation is very low  $\sim 10$  kcal), for which reason only a wall reaction could probably come into consideration for the primary activation of the aldehyde with the "building up" of double bonds. In connection with reaction (5), the deactivation of P'-molecule in collision with oxygen, it is to be noted that it must be introduced because only by chain-breaking with oxygen can the member  $k_5 O_2$  in the denominator of the empirical velocity relation be preserved; otherwise a reaction of that kind would not be likely. As Bodenstein's experiments with renewed oxygen addition after a certain reaction time show, the oxygen inhibition reproduced by this is absolutely certain. It should only be kept in mind that this inhibition is caused not by deactivation but by possible influencing of the wall (page 385). Later experiments by Bodenstein and Jesse<sup>1</sup> have shown that the aldehyde oxidation is greatly dependent during its course on the condition of the wall of the container. In addition, there was a certain induction period even with the purest products; further, an induction period always resulted when no peracetic acid was in the reaction chamber. A great inhibition of the reaction is effected by diethylamine; the effect of aniline, diphenylamine, etc., is not so great.

<sup>1</sup> Jesse, H., Dissertation at Berlin, 1934.

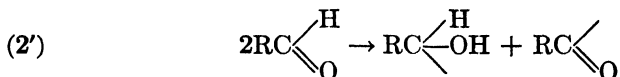


Acetaldehyde oxidation was further investigated by Hatcher, Steacie, and Howland<sup>1</sup> and by Pease.<sup>2</sup> The results of Steacie and his collaborators vary somewhat from those of Bodenstein, but not to an important extent. The reaction velocity is proportional to the 1.7th power of the aldehyde concentration (as opposed to the second power in Bodenstein) and is independent of the oxygen concentration. The differences can probably be attributed to the influence of the wall. According to Steacie, aldehyde oxidation normally shows a decided induction period for the explanation of which he assumes, after similar experiences with propionaldehyde (*cf.* page 389), that the wall prevents the development of chains until it is poisoned by reaction products. In general, the induction period in aldehydes is much less definite than in hydrocarbons; sometimes it is absent altogether. When it is present, however, the general experience is that the reaction is more rapid and that the induction period is shortened or disappears entirely when several experiments are carried out in the same reaction chamber. In any case, therefore, the condition of the wall is a deciding factor. However, it is uncertain whether such places are poisoned by adsorbed reaction products, which would otherwise have broken off chains, or whether, conversely, reaction products<sup>3</sup> remaining adsorbed on the wall are responsible for inducing the reaction chains. By very careful cleansing or long evacuation of the reaction chamber, the influence can again be prevented.<sup>4</sup>

The reaction mechanism suggested by Steacie<sup>5</sup> to explain these phenomena follows Bodenstein's. It is modified only by dropping the member that represents the oxygen inhibition.

A.R. Ubbelohde (cited page 382) assumes that Bäckström's scheme given above for aldehyde oxidation in solution (*cf.* page 382) is also valid for the gas phase, and he also bases upon it particularly hydrocarbon oxidation (*cf.* page 493).

Since the radical appearing in the first reaction continues to react only according to (2), we could, instead of (1) and (2), also consider the reaction



<sup>1</sup> HATCHER, W.H., E.W.R. STEACIE, and HOWLAND, *Can. J. Research*, **5**, 648 (1931); **7**, 149 (1932).

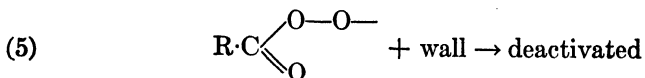
<sup>2</sup> PEASE, R.N., *J. Am. Chem. Soc.*, **55**, 2753 (1933).

<sup>3</sup> Experiments by Jesse support this view (p. 383). According to them, peracetic acid is of influence.

<sup>4</sup> Prettre's experiments on oxygen-hydrogen mixtures are of interest regarding the condition of the wall.

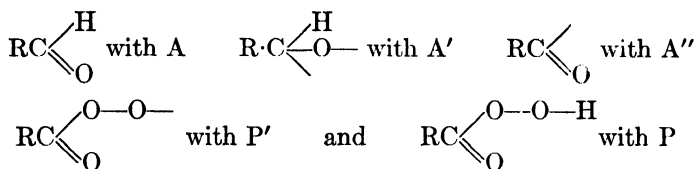
<sup>5</sup> STEACIE, E.W.R., W.H. HATCHER, and S. ROSENBERG, *J. Phys. Chem.*, **38**, 1189 (1934).

and nothing would be formally changed in the result. The above scheme yields a static reaction velocity only if a chain-breaking reaction is added. As such we shall, following Bodenstein, add the deactivation of the peracid radical at the wall



It will be necessary, in addition, to assume that this radical reacts with materials adsorbed at the wall.

If we designate the products appearing in this scheme in the following manner:



The following relations will result from Eqs. (1) to (5) as conditions for stationarity:<sup>1</sup>

$$\frac{d[A']}{dt} = 0 \quad \frac{d[A'']}{dt} = 0 \quad \text{and} \quad \frac{d[P']}{dt} = 0$$

And from this with Eqs. (1) to (5), in which the constants are to be correspondingly numbered,

$$[A'] = \frac{k_1}{k_2} \quad [A''] = \frac{k_1 k_5 [A] + k_1 k_4 [A]^2}{k_3 k_5 [O_2]} \quad [P'] = \frac{k_1 [A]}{k_5}$$

from which the reaction velocity is obtained as follows:

$$\frac{d[P]}{dt} = k_4 [P'] [A] = \frac{k_1 k_4 [A]^2}{k_5} \quad (2)$$

Thus we obtain the dependence on the aldehyde concentration as Bodenstein found it and the independence from the  $O_2$  concentration as Steacie and his associates observed it. The dependence on the 1.7th power of the aldehyde concentration found by Steacie could be interpreted by an influence of the wall condition on one or more of the participating processes. The chain-breaking at the wall, for example, is greatly dependent on the condition of the wall, and the latter as a result of adsorption again is dependent on the composition and pressure of the gases. Further, the reaction (1) is certainly very endothermic (the difference in the energies of the  $\text{>C} = \text{O}$  and of the  $\text{>C} \begin{array}{l} \diagdown \text{O}- \end{array}$  bond might

<sup>1</sup> For computation, cf. Chap. VIII, p. 260.

amount to about 90 (?) kcal). However, since the activation energy of the total reaction amounts to only about 10 kcal, the above mechanism could be brought in harmony with the experiments only if reaction (1) took place in some form at the wall. Then, however, an exact dependence of the total reaction velocity on the second power of the aldehyde concentration could be expected only in case of weak adsorption. By the various surface effects, the inhibition by oxygen observed by Bodenstein and not appearing explicitly in (2) could probably also be explained.

Insofar as the assumption of a chain break (and probably also chain induction) at the wall is correct, a very complicated dependence of the reaction velocity on the condition of the wall as well as of the dimensions of the chamber is to be expected, and this might also explain the partially contradictory experimental results of the various authors.<sup>1</sup>

Semenoff ("Chemical Kinetics and Chain Reactions," page 357) points out that, instead of the velocity expression indicated, the simple expression  $w = \text{const}$  can be applied to Bodenstein's experiments. He gives Table 67 according to an experiment of Bodenstein's; the reaction velocity  $w$  is measured by the change in pressure  $dp/dt$ ;  $[A]$  represents the partial pressure of the aldehyde,  $[O_2]$  that of the oxygen, and  $k$  the constant from Bodenstein's equation

$$w = \frac{dp}{dt} = \frac{k[A]^2}{[O_2] + 150}$$

in which  $[P]$ ,  $[A]$ , and  $[O_2]$  are expressed by the partial pressures at experimental temperature in millimeters of bromonaphthalene.

Actually the velocity itself changes less in the course of the conversion than does Bodenstein's velocity constant  $k$ . Semenoff points out further experiments by Bodenstein in which the reaction velocity seems to be determined more by the alde-

TABLE 67.—ALDEHYDE OXIDATION AT 80°C (FROM BODENSTEIN)

| $t_{\min}$ | $w = dp/dt$ | [A]<br>Bromonaphthalene<br>mm | [O <sub>2</sub> ]<br>mm | $k \cdot 10^4$ |
|------------|-------------|-------------------------------|-------------------------|----------------|
| 120        | 0.175       | 177                           | 127                     | 14             |
| 240        | 0.167       | 157                           | 107                     | 17             |
| 360        | 0.167       | 142                           | 92                      | 20             |
| 420        | 0.167       | 132                           | 82                      | 22             |
| 480        | 0.175       | 122                           | 72                      | 23             |

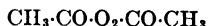
hyde concentration at the beginning of the experiment than by the momentary aldehyde concentration. He thinks, therefore, that the aldehyde oxidation represents a special kind of degenerated explosion like acetylene oxidation but in contrast to that of methane and ethane.

In his book, Semenoff has formally treated cases of explosions in which a constant reaction velocity follows an exponential rise in velocity (the induction period); that

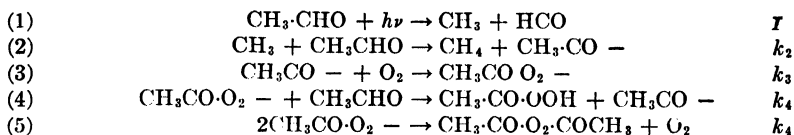
<sup>1</sup> Cf. the effect of a wall coated by KCl on oxidation and the formation of peroxide found by R.N. Pease [*J. Am. Chem. Soc.*, **55**, 2753 (1933)].

would therefore be exactly the same that is observed in the case of acetaldehyde oxidation. How far, however, the special assumptions made in this connection can be realized in nature and whether anything of the sort is present, especially in the case of acetaldehyde, is naturally not indicated by this.

Bowen and Tietz<sup>1</sup> have investigated the oxidation of acetaldehyde in light at room temperature. The reaction velocity was found to be proportional to the root of the light intensity and the first power of the aldehyde concentration, independent of the concentration of the oxygen. As reaction products, peracetic acid and—probably derived from this—diacetyl peroxide appear:



Lewis and v. Elbe,<sup>2</sup> following Bowen and Tietz, give the following scheme, which interprets the findings:



The radical HCO produced according to (1) could likewise continue to react with a fresh aldehyde molecule or also with oxygen. The scheme leads to a velocity expression

$$\frac{d[\text{CH}_3\text{C}(\text{O})\text{OOH}]}{dt} = k_4 \sqrt{\frac{I}{2k_5}} [\text{CH}_3\text{CHO}]$$

in which  $I$  is the number of the light quanta absorbed per second. Such a root relation always results when a molecule under the influence of an absorbed light quantum disintegrates into two fragments whose static concentration is determined by this photodissociation as well as by the recombination. The basic mechanism is quite plausible, and the agreement of the velocity expression derived from it together with experimental findings indicates with considerable certainty that a radical chain mechanism actually is present.

Alcohol inhibits the photochemical aldehyde oxidation in hexane solution; the velocity is then proportional to the first power of the light intensity. Iron carbonyl inhibited the reaction a great deal; when the light was turned on, a white fog appeared. At the end of an induction period, the reaction set in with almost unreduced velocity; in the reaction chamber, a red powder ( $\text{Fe}_2\text{O}_3$ ) was found. This suggests that iron carbonyl is combined in chain-breaking and that when all of it is consumed the reaction takes place just as it would without addition. Selenium diethyl and ethyl iodide inhibited the reaction without causing an induction period.

Lead tetraethyl vapor remained without influence; the latter result is perhaps not entirely unexpected if we know (page 498) that, even at higher temperatures,  $\text{Pb}(\text{eth})_4$  is effective only after it has disintegrated and even oxidized.

The oxidation of acetaldehyde and of benzaldehyde is inhibited by octane, a finding that is interesting because we can understand the action of the higher olefins in oxidation and in knocking only if we

<sup>1</sup> BOWEN, E.M., and E.L. TIETZ, *J. Chem. Soc.*, 1940, p. 234.

<sup>2</sup> "Combustion, Flames and Explosions of Gases," to which we also refer for further discussion.

attribute to them chain-breaking effects (cf. Chap. XII). This assumption is proved directly by existing findings.<sup>1</sup>

**"Cold Flames" in Acetaldehyde.**—Since acetaldehyde is assumed as an intermediary product in hydrocarbon oxidation and its influence on the induction period and the formation of "cold flames" (cf. page 442) has been known, Aivazov<sup>2</sup> investigated the action of acetaldehyde by itself in greater detail, since only qualitative results existed.<sup>3</sup> For these experiments, aldehyde-O<sub>2</sub> mixtures were prepared in the dark, since they easily oxidized in the light even at room temperature. The range for cold flames and for normal ignition is shown for C<sub>2</sub>H<sub>4</sub>O + 0.75O<sub>2</sub> by Fig. 188. Induction periods for cold flames,  $\tau_1$ , as the function of the temperature are shown for the same mixture at 200 mm pressure by Fig. 189. The empirical relation

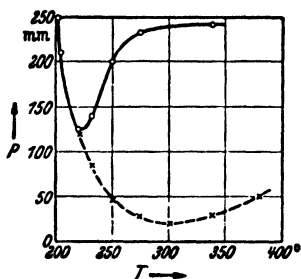


FIG. 188.—Range for cold flames (dashed line) as well as for normal ignition (solid line) for 1 acetaldehyde + 0.75O<sub>2</sub>. (From Aivazov.<sup>4</sup>)

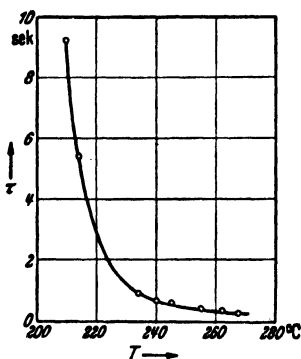


FIG. 189.—Induction periods for the formation of cold flames in 1 acetaldehyde + 0.75O<sub>2</sub> for various temperatures. (From Aivazov.<sup>4</sup>)

$e^{-\gamma/T} \cdot \tau_1 = \text{const}$ , with  $\gamma = 24,000^\circ$  is valid here; the apparent activation energy is thus 48 kcal.

Under certain conditions, the cold flame can pass over into a normal flame, as in hydrocarbon. The induction period observed for the hot flame (from the appearance of the cold flame up to ignition) was rather short ( $< 0.1$  sec) and increased with the temperature while it decreased regularly with the pressure, as it also did with increasing aldehyde concentration.

The reaction outside the range of the cold flames is connected with a drop in pressure. In cold flames, analogous to hydrocarbons, there is a rise in pressure followed by a drop in pressure as the result of cooling, which is followed by a further drop in pressure falling below the initial pressure which must be due to the chemical reaction. In the transition of the cold flames to a normal ignition, a further rise in pressure follows.

<sup>1</sup> PIGULEVSKII, V.V., *J. Gen. Chem. USSR*, **4**, 616 (1934), according to C. Ellis, "The Chemistry of Petroleum Derivatives," New York, 1937.

<sup>2</sup> AIVAZOV, B.V., *Acta Physicochim. URSS*, **8**, 617 (1938).

<sup>3</sup> BARON, M., and P. LAFFITTE, *Compt. rend.*, **205**, 52 (1937).

<sup>4</sup> AIVAZOV, B.V. *Acta Physicochim. URSS*, **8**, 617 (1938).

*c. The Oxidation of Propionaldehyde.*—This reaction, which has been investigated by Steacie and his associates,<sup>1</sup> takes a course similar to the oxidation of acetaldehyde but seems to show fewer complications. It was observed between 120° and 170°C by conducting aldehyde and oxygen separately into a heated pyrex chamber with a content of 200 cm<sup>3</sup> and observing the change in pressure. Altering of the reaction chamber was shown to have no influence on the reaction velocity. If the reaction partners were mixed outside the reaction chamber in the presence of an Hg manometer, the reaction velocity was decreased. The conversion is connected with the decreasing pressure, which at its maximum amounted to about 73 per cent of the aldehyde partial pressure; after that, a slight increase in pressure again appears. The relative decrease in pressure is constant and independent of the experimental conditions if the aldehyde partial pressure is not appreciably under 8 cm Hg and the ratio of O<sub>2</sub>:aldehyde is not appreciably under 1. As the standard of velocity, the time for a pressure decrease

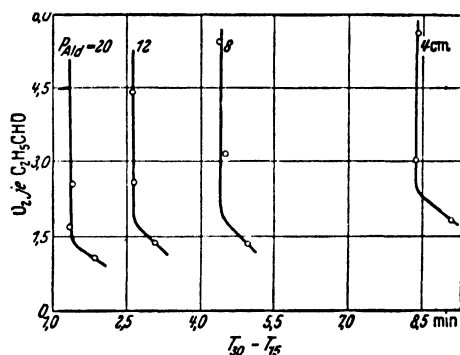


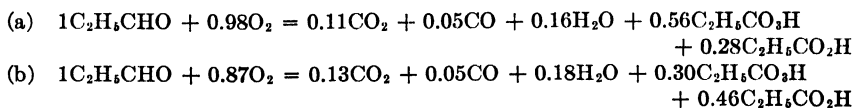
FIG. 190.—Reaction velocity of propionaldehyde with oxygen for various aldehyde pressures (cm Hg). Time in which drop in pressure rises from 15 to 30 taken as a measure of the reaction velocity. (From Steacie.)

of 15 to 30 per cent was taken. Figure 190 gives the reaction velocity at 150.8°C; here  $t_{30} - t_{15}$  (in minutes) is plotted as a function of the relation of oxygen to aldehyde for various aldehyde partial pressures. For  $O_2$  concentrations that are not too low, the reaction velocity can be represented by

$$-\frac{d[\text{C}_2\text{H}_5\text{CHO}]}{dt} = k[\text{C}_2\text{H}_5\text{CHO}]^2$$

The temperature dependence of the reaction velocity was determined for aldehyde partial pressures of 20, 12, and 8 cm Hg; and apparent activation energy of an average of 15.4 kcal resulted.

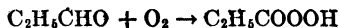
More detailed analyses of the reaction products were also made which, in two experiments with O<sub>2</sub>:aldehyde ratios of 1.16 and 1.35 at 150.8°C, fitted the following conversion equations:



<sup>1</sup> STEACIE, E.W.R., W.H. HATCHER, and S. ROSENBERG, *J. Phys. Chem.*, **38**, 1189 (1934).

Direct titration of the reaction products yielded about one molecule of acid to one molecule of aldehyde that had disappeared. Titration of the iodine liberated by the reaction products from the KI solution (for determining peracids) showed that about 50 per cent of the total acids consisted of peracids.

The chief reaction is therefore



In addition, small quantities of esters were produced. Fichter and Krummenacher<sup>1</sup> has shown that ethyl propionate is a decomposition product of perpropionic acid.

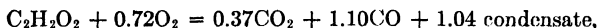
Increasing the surface six times (by packing the reaction chamber with short pieces of pyrex tubing) led to a complete change of the reaction mechanism. The reaction now led to a 15 per cent rise in pressure. In the empty reaction chamber, a rise in pressure finally followed the drop in pressure during which considerable quantities of  $\text{CO}_2$  were produced. In the reaction connected with the rise in pressure in the packed chamber,  $\text{CO}_2$  is likewise preponderantly produced. It is therefore reasonable that this is due in both cases to a surface reaction.

The reaction equation found

$$-\frac{d[A]}{dt} = \text{const } [A]^2$$

can be represented by the scheme indicated earlier (page 386); Steacie himself suggests a somewhat different mechanism (*cf.* the original).

*d. The Oxidation of Glyoxal.*—Glyoxal, a dialdehyde  $\text{CHO}\cdot\text{CHO}$ , appears as the reaction product of the oxidation of acetylene<sup>2</sup> and possibly also plays a role in other oxidation reactions. The investigation of its action in oxidation is therefore of more general interest. The investigation by Steacie, Hatcher, and Horwood<sup>3</sup> showed the following: The reaction, which could be followed from about  $150^\circ$  to  $220^\circ$  and which has been investigated more carefully at the latter temperature, is connected with a rise in temperature dependent on the initial composition and leads to  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and glyoxalic acid as stable terminal products, among which peroxidic substances are proved to be present. The results of a series of analyses can be represented by



in which the condensate consists of water and glyoxalic acid. The reaction was observed by the pressure changes (that this was permissible was proved by special analyses); it shows a short induction period. At the beginning of a series of experiments in a new reaction chamber, a decided aging effect of the surfaces could be noted; the reaction velocity rose from experiment to experiment and was constant only after about 30 measurements. This is an effect noted again and again in the oxidation of organic substances. For the reaction velocity, the following empirical expression was found:

$$-\frac{d[\text{C}_2\text{H}_2\text{O}_2]}{dt} = \text{const } [\text{C}_2\text{H}_2\text{O}_2]^{1.6}$$

<sup>1</sup> FICHTER and KRUMMENACHER, *Helv. Chim. Acta*, **1**, 146 (1918).

<sup>2</sup> KISTIAKOWSKY, G.B., and S. LENHER, *J. Chem. Soc.*, **52**, 3785 (1930). KISTI-KOWSKY, *J. Chem. Soc.*, **52**, 4837 (1930). LENHER, S., *J. Chem. Soc.*, **53**, 2962 (1931).

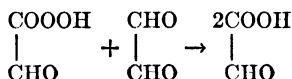
<sup>3</sup> STEACIE, E.W.R., W.H. HATCHER, and J.F. HORWOOD, *J. Chem. Phys.*, **3**, 551 (1935).

Here the standard of velocity chosen was the time during which the increase in pressure rose from 20 to 40 per cent; at 220°, a glyoxal pressure of 20 cm Hg, and a ratio of  $O_2:C_2H_2O_2 = 1.19$ , the time required was about 7.5 min.

By packing of the reaction chamber with pieces of pyrex tubing, the course of the reaction is again considerably changed. With an enlargement of the surface by five to six times, the reaction velocity dropped by about half. At the same time, the rise in pressure at completed reaction is reduced and the ratio  $CO:CO_2$  in the gaseous reaction products is reduced from about 3.0 to 1.7.

Steacie and his associates conclude, from the relatively weak reduction of the reaction velocity by packing and from the fact that additions of nitrogen do not noticeably accelerate the reaction velocity, that the wall is not the essential chain-breaking factor. According to the results of Kassel and Storch (cited page 273) and Lewis and v. Elbe (cited page 273), which were not yet known at the time of Steacie's work and which deal with the influence of the wall and its small chain-breaking effect (cf. Chap. VIII, page 276), these deductions are not conclusive. Rather the diffusion of active particles to the wall with very small breaking probability at the wall is no longer velocity determining, and the reaction velocity is therefore independent also of the addition of foreign gases even if the chains are broken exclusively at the wall. Bodenstein and Winter<sup>1</sup> were able to show that a similar situation prevails in chlorine-oxygen-hydrogen reactions. Foreign gases were ineffectual in spite of chain-breaking at the wall. The breaking probability per impact on the wall,  $\epsilon$ , was found to be  $\sim 10^{-4}$ .

The following reaction is suggested for the formation of glyoxylic acid: A peracid that is formed in the primary stages and cannot be isolated reacts according to



That oxalic acid does not appear as a reaction product is in agreement with experiments by Hatcher and Holder<sup>2</sup> on the oxidation of glyoxylic acid in solution with  $H_2O_2$  in which no traces whatever of oxalic acid appear.

The reaction mechanism is assumed to be analogous to that of other aldehydes.

*e. General Remarks on Aldehyde Oxidation.*—We shall discuss the conditions in the oxidation of higher aldehydes in connection with hydrocarbon oxidation. We can put down the following as the general result of the investigation of the oxidation in lower aldehydes: Even for these simplest of oxidation reactions of organic material in the gas phase, the mechanism cannot be regarded as having been clarified in all its details. The difficulties, however, lie in the nature of the case—multiplicity of the possible reaction products, both intermediary and terminal, non-predictability of the wall influences, and impossibility of a direct observation of short-lived, active intermediary products. Since there is no prospect of an elimination of these difficulties in the near future, this condition must simply be accepted and an attempt made to look for laws that can be stated without special assumptions on the nature of

<sup>1</sup> BODENSTEIN and WINTER, *Ber. preuss. Akad. Wiss.*, 1936, I.

<sup>2</sup> HATCHER, W.H., *Trans. Roy. Soc. Can.*, (3), 19, 11 (1925)..



the intermediary reaction products, or at least with a minimum of such assumptions.

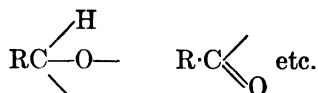
On the one hand, the formal mechanism is to be explained, namely, a reaction velocity almost independent of the oxygen concentration, perhaps even inhibited by oxygen as well as by dependence on about the second power of the aldehyde concentration, characteristics that will recur in a similar manner in many oxidation reactions of organic materials. On the other hand, the observed influences of the wall must be taken into account, namely, (a) perhaps a catalytic reaction at the wall that can lead to products other than oxidation in the gas phase and (b) an influence of the chain reaction in the gas phase by chain induction and/or chain-breaking at the wall. For the first, we shall have to content ourselves with giving the influence of the wall qualitatively, since the experimental material does not justify any further conclusions. It can be assumed as fairly certain that we are dealing with chain reactions in the oxidation of organic material. In aldehyde oxidation in solution, this may be considered absolutely certain. For the gas phase, hardly any doubt exists, since we have reported so much material—the wall influence alone is quite convincing—and further facts will be found in the following pages.

The assumption that free radicals decidedly take part in the reaction chain seems plausible but has of course not been proved. It might be difficult to prove directly, because a spectroscopic proof for the small concentrations to be expected is difficult and might be rendered completely impossible by the auto-absorption of the aldehyde in the ultra-violet as well as by the absorption of the peracids and other reaction products.<sup>1</sup> There is, however, a considerable amount of indirect evidence for a participation of radicals. Fundamentally only products that are slow to react survive as stable products and can be submitted to analyses. Those products, therefore, which can be proved to be present are the very ones that are of minor importance as active intermediary products. Free radicals, however, certainly play a role as active intermediary products in many disintegration reactions of organic materials,<sup>2</sup> as can be seen from both photochemical experiments and experiments with added parahydrogen (*cf.* in this connection page 371). On the other hand, in the oxidation of hydrogen, it is quite certain that free radicals take part, H-atoms and O-atoms, the radicals OH and HO<sub>2</sub>. For high temperatures, the participation of H and OH is directly proved (pages 321ff.). Since in addition the oxidation of oxygen-

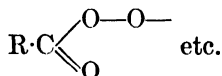
<sup>1</sup> For absorption of the individual substances and reaction products, *cf.* Egerton as well as A.R. Ubbelohde, cited p. 399.

<sup>2</sup> *Cf.* the compilation by L. v. Müffling and R. Maess, *Z. Elektrochem.*, **44**, 428 (1938).

hydrogen has, in its entire behavior, much in common with the oxidation reactions of organic materials, the conclusion is at least reasonable that free radicals also take part here. Since, further, peroxidic substances especially at low temperatures are to be regarded as reaction products, the assumption made by almost all authors that radicals attach molecular oxygen to a peroxide radical likewise has much in its favor. With all this, however, nothing is said about the structure of these radicals. In the following, without expressly mentioning these reservations, we shall operate with radicals as they are assumed by Bodenstein, A.R. Ubbelohde, the author, Lewis and v. Elbe, and others, namely,

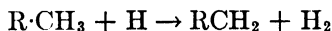


which then react further to

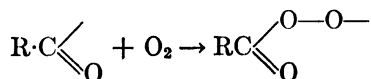


It must be emphasized, however, that the essential point is whether the radicals participate and their reaction with oxygen, not the special structure of the radicals. Insofar as it should seem practical in the course of future investigations to introduce radicals of somewhat varying structure, most of the conclusions here drawn will continue to stand. In the following section, we shall present what is known about the energies of individual bonds of organic molecules and the most probable energies of various radicals, from which the estimates of the heat energies of the individual radical reactions will then be obtained.

As plausible reactions, only those will be admitted which on the one hand are reasonable in energy and which on the other hand do not contain any too complicated rearrangements in a single stage. Thus, for example, conversions like the following are plausible:



or the reaction assumed earlier



(perhaps in a triple collision) and similar conversions. In the latter case, it should be considered whether the attachment can take place in a double collision or whether, as is the case without exception in the recombination of atoms, a triple-collision partner is necessary that is able to take up a part of the reaction energy. According to theoretical

considerations by Kimball,<sup>1</sup> which are convincing in themselves, a triple-collision partner can be the more readily dispensed with the more complicated the molecule, because the reaction energy can be distributed over a great number of internal degrees of freedom. It will therefore be necessary to take into account the possibility of double-collision association in the recombination of organic radicals and perhaps also in the attachment of molecular oxygen to them.

Reactions like a "hydroxylation" according to Bone, that are produced by reaction with molecular oxygen in one division from the original molecule of a hydrocarbon hydroxylated product like



must be viewed as decidedly improbable. Reactions of that kind can certainly be eliminated from a list of conceivable intermediary reactions.

As a conclusion from the experiments on aldehyde oxidation, which we shall utilize for the oxidation of hydrocarbons, we can, we think, assume that (1) there is a chain reaction, (2) free radicals probably participate in this chain reaction, and (3) one or more of these radicals react with molecular O<sub>2</sub> to form peroxide radicals that take a decisive part in the course of the reaction. The wall, probably in several respects, plays an essential role under the conditions of slow oxidation, but quantitative data are for the present out of the question.

**3. Decomposition of Carbohydrates, as Well as of Intermediate Products of Combustion. Absorption Spectra.** *a. Decomposition of Organic Matter.*<sup>2</sup>—Since almost all organic compounds disintegrate in themselves at the temperatures reached during oxidation of carbohydrates and especially in the flame, we must also be informed about reactions of decomposition of these elements if we want to determine which processes may take place simultaneously. In general, the decomposition will remain influenced by simultaneously occurring disintegrating processes, as well as by reactions of oxidations.<sup>3</sup> Where experiences are available, they show that the spontaneous decomposition can be speeded up only by such simultaneous processes which under certain circumstances are connected with the production of free radicals. It would therefore be permissible to regard the speed, which was found for the decomposition of pure substances, as the minimum speed in general with which these substances disintegrate during oxidation. The decomposition of especially complicated organic molecules in general does not occur in a single step to the stable end products

<sup>1</sup> KIMBALL, *J. Chem. Phys.*, **5**, 310 (1937).

<sup>2</sup> For observations of the decomposition of organic matter in regard to knock resistance and ignitibility in the Diesel engine, cf. G.D. Boerlage and W.J.D. Van Dyck, *J. Inst. Petroleum Tech.*, **21**, 40 (1935). Also F.O. Rice, *Ind. Eng. Chem.*, **27**, 915 (1935).

<sup>3</sup> According to F.O. Rice (lecture for the Faraday Society August, 1939), the decomposition of carbohydrates is catalyzed through small amounts of oxygen, as particularly shown with butane.

but passes through intermediate products, in which free radicals frequently play a part.<sup>1</sup>

We can gain a certain insight into the possibilities of the formation of free radicals if we know the energies of the individual bonds in the molecules. With the knowledge of these bond energies, we can evaluate the quantities of heat developed in the supposed radical reactions for the mechanism of reaction—of the decomposition as well as of the oxidation—for which reason we insert here a table of bond energies. These bond energies are therefore those energies, which must be supplied if the molecule is to be split at the respective bond.

TABLE 68.—BOND ENERGIES

|  |                    |   |            |
|--|--------------------|---|------------|
| $\text{H}_2 \rightarrow 2\text{H}$   | 102.7 kcal         | $\text{C}=\text{C} \rightarrow \text{C} + \text{C}$             | ~ 125 kcal |
| $\text{O}_2 \rightarrow 2\text{O}$   | 116.4 kcal         | $\text{C}\equiv\text{C} \rightarrow \text{C} + \text{C}$        | ~ 164 kcal |
| $\text{CO} \rightarrow \text{C} + \text{O}^*$  | (160 or 202 kcal)† | $\text{C}-\text{O} \rightarrow \text{C} + \text{O}$             | ~ 75 kcal  |
| $\text{H}_2\text{O} \rightarrow \text{H} + \text{OH}$                                | ~ 117.8 kcal       | (Alcohols, ether)   | —          |
| $\text{H}_2\text{O}_2 \rightarrow 2\text{OH}$  | 52 kcal            | $\text{C}_{\text{ar}}-\text{O} \rightarrow \text{C} + \text{O}$ | ~ 97 kcal  |
| $\text{HO}_2 \rightarrow \text{H} + \text{O}_2$                                      | ~ 40 kcal          | (Phenols)   | —          |
| $\text{O}_3 \rightarrow \text{O} + \text{O}_2$                                       | 24 kcal            | $\text{C}=\text{O} \rightarrow \text{C} + \text{O}$             | ~ 165 kcal |
| $\text{C}_{\text{al}}\text{H}^3 \rightarrow \text{C} + \text{H}$                     | ~ 93 kcal          | (Aldehydes, ketones)  | —          |
| $\text{C}_{\text{ar}}\text{H} \rightarrow \text{C} + \text{H}$                       | ~ 102 kcal         | —   | —          |
| $\text{C}_{\text{al}}-\text{C}_{\text{al}} \rightarrow \text{C} + \text{C}$          | ~ 71 kcal          | —   | —          |
| $\text{C}_{\text{ar}}-\text{C}_{\text{ar}} \rightarrow \text{C} + \text{C}^\ddagger$ | ~ 96 kcal          | —   | —          |
| $\text{C}_{\text{al}}-\text{C}_{\text{ar}} \rightarrow \text{C} + \text{C}$          | ~ 80 kcal          | —   | —          |

\* According to photochemical experiments by Faltings, Groth, and Hartek [cf. the compilation by W. Groth, *Z. Elektrochem.*, **45**, 270 (1939)], the bond energy of CO is to be found between 193 and 219 kcal.

† It has not been possible as yet to establish definitely the dissociation energy of CO.

‡ The energy  $\text{C}_{\text{al}}\text{H}$  is therefore the energy that is necessary to separate an H-atom from an aliphatic molecule, e.g., ethane; correspondingly  $\text{C}_{\text{ar}}\text{H}$  is the separation work of an H-atom from an aromatic molecule, e.g., benzol. Correspondingly  $\text{C}_{\text{al}}-\text{C}_{\text{al}}$  is the bond stability between two C-atoms in an aliphatic molecule, e.g., ethane;  $\text{C}_{\text{ar}}-\text{C}_{\text{ar}}$  correspondingly that in benzol.  $\text{C}_{\text{ar}}-\text{C}_{\text{al}}$  is the energy required to split the  $\text{CH}_3$  group from the benzol nucleus of the toluol.

On the whole, it must be said that the energy of the bond of two atoms in an organic molecule naturally is not completely independent of what bonds the atoms have already established. Aside from certain exceptions, the assumption of constant bond energies is a rather good approximation, of which good use can be made. The values of Table 68, taken from an older summary by Grimm and Wolf for the organic molecules, are really out of date, because older values of the heat of sublimation of the carbohydrates were used for their calculation. Since there are no newer estimations that have led to well-defined results, however, we shall continue for the present to use older ones, which are probably sufficiently exact for relative values.

Generally a strengthening of the bond takes place if several equivalent valences exist for one bond. Thus, for instance, in a radical like  $\text{CH}_2-\text{CH}=\text{CH}_2$ , which we could just as well ascribe the structure  $\text{CH}_2=\text{CH}-\text{CH}_2$ , the bonds are strengthened.<sup>2</sup>

<sup>1</sup> MAESS, R., and L. v. MÜFFLING, *Z. Elektrochem.*, **44**, 428 (1938). STEACIE, E.W.R., *Chem. Rev.*, **22**, 311 (1938). SCHUMACHER, H.J., "Chemische Gasreaktionen," 1938. RICE, F.O., and K.K. RICE, "The Aliphatic Free Radicals," Johns Hopkins Press, Baltimore, 1935.

<sup>2</sup> As can be proved directly through experiment.

The consequence of this is that larger molecules containing double bonds disintegrate most easily, when such especially stable products can be formed, *e.g.*,



at the dotted line. This is Schmidt's<sup>1</sup> rule of double bonds, according to which molecules with double bond disintegrate most easily at the alternate single bond calculated from the double bond. The effect of the inhibiting reaction of olefins, frequently observed, could be explained by the fact that, in the reaction of paraffinic

TABLE 69.—DISINTEGRATION CONSTANTS OF PARAFFINS (FROM A COMPILATION BY STEACIE)

| Material                                 | log <i>A</i> | <i>E</i> , kcal/mol | <i>k</i> <sub>425</sub> | <i>k</i> <sub>575</sub>    | Author                              |
|--|--------------|---------------------|-------------------------|----------------------------|-------------------------------------|
| CH <sub>4</sub>                          | 12.00        | 79,385              | 1.3 · 10 <sup>-13</sup> | 3.3 · 10 <sup>-9</sup>     | Kassel <sup>1</sup>                 |
| C <sub>2</sub> H <sub>6</sub>            | 15.12        | 73,200              | 1.5 · 10 <sup>-8</sup>  | 1.7 · 10 <sup>-4</sup>     | Marek and McCluer <sup>2</sup>      |
|  | 16.06        | 77,700              | 5.1 · 10 <sup>-9</sup>  | 1.0 · 10 <sup>-4</sup>     | Newly computed <sup>3</sup>         |
|  | 14.1         | 69,800              | 1.6 · 10 <sup>-8</sup>  | 1.2 · 10 <sup>-4</sup>     | Sachsse <sup>4</sup>                |
|  |              | (65,000)            |                         | 1.0 · 10 <sup>-4</sup>     | Storch and Kassel <sup>5</sup>      |
|  |              |                     |                         |                            | Pease and Durgan <sup>6</sup>       |
| C <sub>3</sub> H <sub>8</sub>            |              |                     |                         | 1.5 · 10 <sup>-3</sup>     | Frey and Hepp <sup>7</sup>          |
|  | 13.44        | 62,100              | 9.6 · 10 <sup>-7</sup>  | 2.6 · 10 <sup>-3</sup>     | Marek and McCluer <sup>2</sup>      |
|  | 16.60        | 74,850              | 1.4 · 10 <sup>-7</sup>  | 1.9 · 10 <sup>-3</sup>     | Paul and Marek <sup>3</sup>         |
|  |              | (65,000)            |                         |                            | Pease and Durgan <sup>6</sup>       |
|  | 13.53        | 61,400              | 1.9 · 10 <sup>-6</sup>  | 4.8 · 10 <sup>-3</sup>     | Frey and Hepp <sup>7</sup>          |
| <i>n</i> -C <sub>4</sub> H <sub>10</sub> | 17.05        | 73,900              | 7.8 · 10 <sup>-7</sup>  | 9.8 · 10 <sup>-3</sup>     | Paul and Marek <sup>3</sup>         |
|  | 12.54        | 58,700              | 1.5 · 10 <sup>-6</sup>  | 2.6 · 10 <sup>-3</sup>     | Steacie and Puddington <sup>8</sup> |
|  |              | (65,000)            |                         |                            | Pease and Durgan <sup>6</sup>       |
| iso-C <sub>4</sub> H <sub>10</sub>       |              |                     |                         | 4.8 · 10 <sup>-3</sup>     | Frey and Hepp <sup>7</sup>          |
|  | 14.89        | 66,040              | 1.5 · 10 <sup>-6</sup>  | 7.1 · 10 <sup>-3</sup>     | Paul and Marek <sup>3</sup>         |
| <i>n</i> -C <sub>5</sub> H <sub>12</sub> | 13.4         | 61,200              | 2.4 · 10 <sup>-6</sup>  | 5.7 · 10 <sup>-3</sup>     | Frey and Hepp <sup>7</sup>          |
| iso-C <sub>5</sub> H <sub>12</sub>       | 12.93        | 58,600              | 3.7 · 10 <sup>-6</sup>  | 6.5 · 10 <sup>-3</sup>     | Frey and Hepp <sup>7</sup>          |
|  | 12.43        | 55,500              | 1.1 · 10 <sup>-5</sup>  | 1.3 · 10 <sup>-2</sup>     | Frey and Hepp <sup>7</sup>          |
| <i>n</i> -C <sub>6</sub> H <sub>14</sub> | 14.58        | 64,500              | 2.3 · 10 <sup>-6</sup>  | 8.7 · 10 <sup>-3</sup>     | Dinces <i>et al.</i> <sup>9</sup>   |
| 2,3-Dimethylbutane                       |              |                     |                         | 1.9—2.4 · 10 <sup>-2</sup> | Frey and Hepp <sup>7</sup>          |
| <i>n</i> -C <sub>7</sub> H <sub>16</sub> | 9.85         | 46,500              | 1.9 · 10 <sup>-5</sup>  | 7.1 · 10 <sup>-3</sup>     | Pease and Morton <sup>11</sup>      |
| <i>n</i> -C <sub>8</sub> H <sub>18</sub> | 14.70        | 64,900              | 2.3 · 10 <sup>-6</sup>  | 9.1 · 10 <sup>-3</sup>     | Dinces <i>et al.</i> <sup>10</sup>  |

<sup>1</sup> KASSEL, L.S., *J. Am. Chem. Soc.*, **54**, 3949 (1932).

<sup>2</sup> MAREK and MCCLUER, *Ind. Eng. Chem.*, **23**, 878 (1931).

<sup>3</sup> PAUL and MAREK, *Ind. Eng. Chem.*, **26**, 454 (1934).

<sup>4</sup> SACHSSE, H., *Z. physik. Chem.*, Sec. B, **31**, 87 (1935).

<sup>5</sup> STORCH, H.H., and L.S. KASSEL, *J. Am. Chem. Soc.*, **59**, 1240 (1937).

<sup>6</sup> PEASE, R.N., and DURGAN, *J. Am. Chem. Soc.*, **52**, 1262 (1930).

<sup>7</sup> FREY and HEPP, *Ind. Eng. Chem.*, **25**, 441 (1933).

<sup>8</sup> STEACIE, E.W.R., and PUDDINGTON. Unpublished work.

<sup>9</sup> DINCES and FROST, *J. Gen. Chem. USSR*, **4**, 610 (1934).

<sup>10</sup> DINCES and ZHERKO, *J. Gen. Chem. USSR*, **6**, 68 (1936).

<sup>11</sup> PEASE, R.N., and MORTON, *J. Am. Chem. Soc.*, **55**, 3190 (1933).

<sup>1</sup> SCHMIDT, O., supported by T. Foerster, *Z. Elektrochem.*, **43**, 667 (1937).

radicals with olefins, such especially stable and consequently sluggish radicals are formed. It could also be explained, of course, by accretion of intermediary radicals to the double bond.

If a disintegration of organic molecules results in free radicals, it will occur at the weakest place of the molecule, *i.e.*, with paraffins at the C—C bond, with olefins according to the rule of the double bond. To a certain extent, the disintegration of organic molecules certainly takes place by way of free radicals;<sup>1</sup> and we should take into account the possibility that, especially at higher temperatures, the free radicals thus formed play a part in the introduction of the chain reaction of oxidation.

The thermal disintegration of paraffins can in general be described by a time relation of the first order, even though the mechanism is by no means always that of a simple monomolecular reaction. Lower paraffins, olefins, and hydrogen occur as end products of the disintegration, and besides them occasionally also higher olefins in consequence of a polymerization of base olefins.

For judging the speed of disintegration of paraffins, we give a summary from Steacie (cited page 395) for the constants of disintegration of the first order:

$$k = Ae^{-E/RT}$$

The values are not all quite reliable and are not absolutely comparable. Especially the wider variations in the factor *A* (and the corresponding variations in *E*) might not all be reliable, but they are useful anyway for orientation. Besides these, there are constants of disintegration given according to Steacie for 425° and 575°.

Directly measured values computed for the disintegration of the first order are presented in Table 70, which follows.<sup>2</sup>

The disintegration of olefins has often been investigated, but there are few reliable disintegration constants and measured activation energies.

TABLE 70.—DISINTEGRATION CONSTANTS OF HYDROCARBONS, SEC<sup>-1</sup>

| Material                          | Temperature, °C         |                             |                            |                            |                            |                        |
|-----------------------------------|-------------------------|-----------------------------|----------------------------|----------------------------|----------------------------|------------------------|
|                                   | 570°                    | 590°                        | 620°                       | 660°                       | 700°                       | 760°                   |
| <i>n</i> -Octane.....             | 3.9 · 10 <sup>-2</sup>  | 8.1 · 10 <sup>-2</sup>      | 24 · 10 <sup>-2</sup>      | —                          | —                          | —                      |
| <i>n</i> -Heptane.....            | 2.2 · 10 <sup>-2</sup>  | 4.7 · 10 <sup>-2</sup>      | 14.6 · 10 <sup>-2</sup>    | —                          | —                          | —                      |
| <i>n</i> -Hexane.....             | 1.0 · 10 <sup>-2</sup>  | 2.1 · 10 <sup>-2</sup>      | 6.2 · 10 <sup>-2</sup>     | —                          | —                          | —                      |
| Iso-octane <sup>1</sup> .....     | 3.9 · 10 <sup>-2</sup>  | 8.1 · 10 <sup>-2</sup>      | 24 · 10 <sup>-2</sup>      | —                          | —                          | —                      |
| Di-isobutylene <sup>1</sup> ..... | 14.4 · 10 <sup>-2</sup> | (29.9 · 10 <sup>-2</sup> )* | (89.4 · 10 <sup>-2</sup> ) | —                          | —                          | —                      |
| Cyclohexane.....                  | —                       | —                           | (0.32 · 10 <sup>-2</sup> ) | 2.3 · 10 <sup>-2</sup>     | 16.7 · 10 <sup>-2</sup>    | —                      |
| Benzol.....                       | —                       | —                           | —                          | (0.13 · 10 <sup>-2</sup> ) | (0.34 · 10 <sup>-2</sup> ) | 1.5 · 10 <sup>-2</sup> |

<sup>1</sup> Iso-octane = 2,2,4-trimethyl pentane; di-isobutylene is a mixture of two isomeric olefins passing over into iso-octane by hydration.

\* The numbers in parentheses are extrapolated values.

On the whole, olefins are less stable than the corresponding paraffins; we can use the relation of di-isobutylene and iso-octane in the above table for an evaluation. We also give some values from Schumacher (cited page 395) and from v. Müffling and Maess (cited page 395) for the disintegration of oxygen-containing combinations,

<sup>1</sup> RICE, F.O., cited p. 395. MAESS and v. MÜFFLING, cited p. 395. STEACIE, cited p. 395.

<sup>2</sup> From JOST, W., L. v. MÜFFLING, and W. ROHRMANN, *Z. Elektrochem.*, **42** (1936).

which always occur as intermediate products of oxidation and whose behavior we must therefore know. The disintegration of formaldehyde can be obtained through an equation of the second order with an activation energy of 44.5 kcal; at 842° abs and at 371 mm Hg initial pressure, the half-life for the disintegration is 69 sec. In the presence of ether formaldehyde, disintegration is fifteen times faster than in the case of auto-disintegration, as a consequence of the appearance of free radicals (from Fletcher and Rollefson). Carbon monoxide and hydrogen appear as products of reaction.<sup>1</sup>

Acetaldehyde disintegrates in CO and CH<sub>4</sub>; the energy of activation for the disintegration amounts to about 46 kcal. The reaction does not take its course according to a simple order; according to Fletcher and Hinshelwood, at 829° abs. at 130 or 415 mm initial pressure, the half-life periods for the deterioration amount to, respectively, 196 and 111 sec.

Methanol disintegrates into carbon monoxide and hydrogen, as a velocity constant of the first order is valid

$$k = 1.7 \cdot 10^{13} e^{-68,000/RT} \text{sec}^{-1}$$

For butyl alcohol

$$k = 4.8 \cdot 10^{14} e^{-65,500/RT} \text{sec}^{-1}$$

The disintegration of lower alcohols progresses in general under H<sub>2</sub> splitting and formation of the corresponding aldehydes, which under certain circumstances disintegrate still more. With higher alcohols, the disintegration in H<sub>2</sub>O and olefins predominates.

A series of ethers has also been investigated with respect to disintegration. The disintegration constant of Diethyl ether is

$$k = 3.2 \cdot 10^{11} e^{-53,000/RT} \text{sec}^{-1}$$

For acetone

$$k = 1.5 \cdot 10^{15} e^{-68,500/RT} \text{sec}^{-1}$$

Since organic nitrates accelerate the oxidation of hydrocarbons and therefore the knocking as well as the ignition in the Diesel engine, it should be stated for orientation that the disintegration constant of ethyl nitrite is

$$k = 1.3 \cdot 10^{14} e^{-37,700/RT} \text{sec}^{-1}$$

Since we shall use all these data only for the orientation about the stability of eventual products, we do not need to go into details here about the decrease in speed toward lower pressures generally observed with monomolecular reactions (Schumacher, cited page 395).

The disintegration of organic compounds takes place at least in part through free radicals whose appearance might be of importance for the introduction of reactions of oxidation (v. Müffling, Maess, and Steacie, cited page 395).

*b. Absorption Spectra of Organic Compounds, Especially of Intermediate Products and Products of Reaction in Combustion.*—Egerton and Pidgeon<sup>2</sup> have investigated the absorption spectra of hydrocarbons in combustion, at temperatures varying between about 250° and 450°, with air, flowing through an absorption tube. Aldehydes were observed here, especially formaldehyde, and further a continuous absorption in

<sup>1</sup> For disintegration of acrolein, compare H.W. Thompson and J.J. Frewing, *J. Chem. Soc.*, 1935, p. 1443; a more recent examination about the disintegration of butane in L.S. Echols and R.N. Pease, *J. Am. Chem. Soc.*, **61**, 208 (1939).

<sup>2</sup> EGERTON, A.C., and L.M. PIDGEON, *Proc. Roy. Soc. London, A*, **142**, 26 (1933).

the extreme ultraviolet, which, at least in part, is conditioned by organic acids produced in the oxidation. During the period of induction, no absorption was observed. A band at about 2600 Å occurs with higher hydrocarbons, beginning with butane, and appears first before the aldehyde bands. With the combustion of corresponding aldehydes, the band of this unknown substance X does not occur.

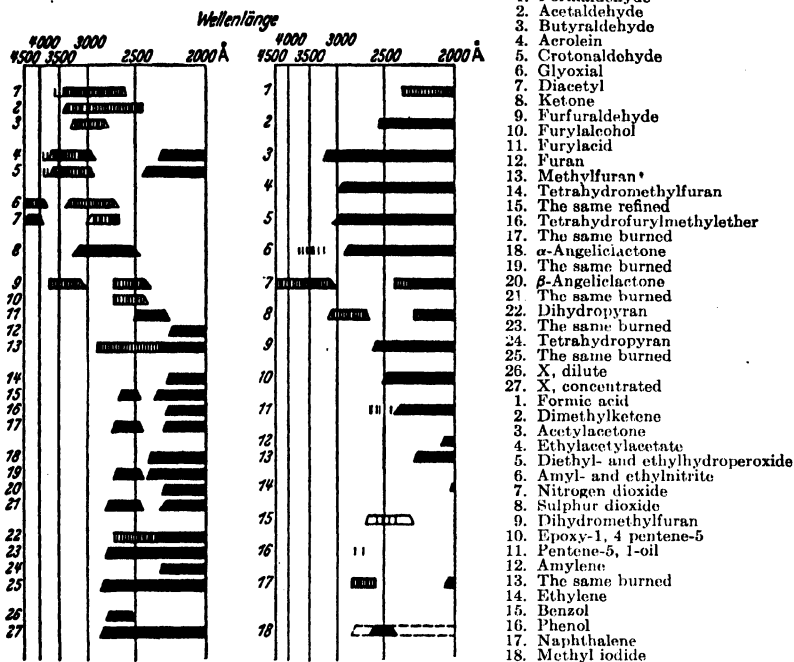


Fig. 191.—Absorption spectra in the ultraviolet. (Vertically shaded = bands. Black surfaces = continuous absorption.) (From Ubbelohde, London, p. 393.)

Ubbelohde<sup>1</sup> has undertaken detailed examinations with the aim of clearing up the nature of the band substance X. He has taken absorption spectra of a large number of organic substances, which we reproduce in Fig. 191 in the schematic representation from Ubbelohde (vertically hatched areas signify bands; black surfaces, continuous absorption).

Ethyl nitrite and NO<sub>2</sub> lower the temperature at which the X-bands appear in burning hydrocarbon-air mixtures, but they do not change the general course. No X-band appeared with butylenes and amylenes, and just as little in the breaking of the butyl chain as in ethyl ether, in spite of its low combustion temperature.

Ranges resembling those of the X-band were obtained with the combustion of ether of tetrahydrofuryl alcohol and  $\alpha$ - and  $\beta$ -angelicalactones. None of the stable compounds examined showed a band

<sup>1</sup> UBBELOHDE, A. R., *Proc. Roy. Soc. London, A*, **152**, 378 (1935).

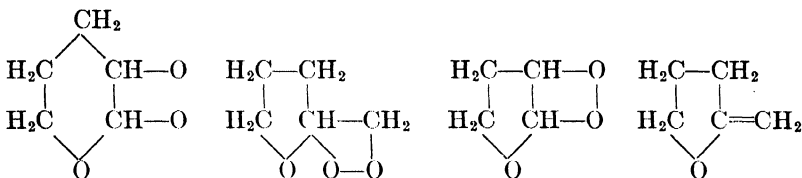


(aside from methyl iodide, which naturally does not come into consideration) that corresponded to the X-band. X is therefore a product of combustion of the paraffins and possibly of a number of oxygen-ring compounds like unsaturated lactones and tetrahydrofurfuryl ether.

Ubbelohde also examined chemically the occurring intermediate products (we must refer you to the original for the method) in an apparatus resembling that used by Mondain-Monval.<sup>1</sup>

Condensed products of combustion from pure hexane resulting from combustion at 300° separated into a hydrocarbon and an aqueous phase that smelled of burned sugar and aldehydes. The aqueous layer showed an especially strong peroxide reaction; in the same manner, its vapors showed much more strongly the X-bands in absorption. The substance X must therefore be sufficiently stable in solution.

Furthermore, O-ring compounds from the hexane layer were demonstrated; with pentane, they demonstrated unsaturated, dihydropyran, methyl tetrahydrofuran, ethanol (?), hydroxy acids, aldehydes, alcohols, ketones only in traces, and furthermore peroxides, probably olefin peroxides.<sup>2</sup> Probably peroxides in question are



Epoxy-1, 4-pentene-5

peroxidates so easily when oxygen is conducted through at the boiling point that a dense fog of peroxide is formed, just as with the slow combustion of pentane. Analogous observations have often been reported with hydrocarbon oxidation. Ubbelohde assumes that X takes its origin in the disintegration of peroxides; ascorbic acid gives practically the same band as X.

**4. The Oxidation of the Lowest Hydrocarbons (Acetylene, Ethylene, Methane, Ethane, Propane).** *a. The Oxidation of Acetylene.*—With the oxidation of unsaturated lower hydrocarbons, we expect that the multiple bond, as the weakest place in the molecule, will be attacked by oxygen, and we could therefore think of more simple conditions than those with saturated hydrocarbons. In spite of this, reactions like  $C_2H_2 + O_2 \rightarrow CHO \cdot CHO$ , the direct formation of glyoxal from acetylene, or  $C_2H_4 + O_2 \rightarrow 2HC \cdot HO$ , the conversion of ethylene with oxygen to formaldehyde, cannot be the decisive reaction stages in these oxidation processes, even

<sup>1</sup> MONDAIN-MONVAL, P., and QUANQUIN, *Ann. chim. phys.*, **15**, 309 (1931).

<sup>2</sup> For the analysis of products of reaction, compare among others S. Estradère, *Pub. sci. tech. ministère air France*, **49**, 1934. GIORGIO, R., *Gaz. chim. ital.*, **64**, 564 (1934).

if the corresponding products appear. Aside from the basis of other criteria, which we shall discuss later, this is already excluded by the fact that the corresponding oxidation reactions show all the characteristics of chain reactions, whereas the above transformations are not chain reactions. We shall see that we are compelled also in the case of these reactions to accept some kind of variation of Bodenstein's mechanism, which Bodenstein himself has already applied to the oxidation of acetylene.<sup>1</sup>

The oxidation of acetylene has been examined by Kistiakowsky and collaborators<sup>2</sup> as well as by Steacie and McDonald.<sup>3</sup> Bone and Andrew<sup>4</sup> had already examined the slow oxidation of acetylene between 200° and 350° and had found carbon monoxide and formaldehyde as the chief products of reaction. The liquid products that are formed by the effect of ozone on acetylene consist mainly of glyoxal, CHO-CHO.<sup>5</sup>

Kistiakowsky and Lenher examined the oxidation of acetylene in a flow system at atmospheric pressure. Purified acetylene and oxygen were introduced into the heated reaction chamber at a moderate rate, the liquid products of reaction were frozen out with solid CO<sub>2</sub>, and the gaseous products were collected directly. A summary of the analysis values will be found in Table 71 (for the method, we refer to the original). The experiments were made in a pyrex vessel 22 mm in diameter and 78 cm<sup>3</sup> in volume; the velocity of flow was such that, for 290°C, a duration of ~ 200 sec resulted. Qualitatively glyoxal was also detected among the products of reaction.

TABLE 71.—AVERAGE RESULTS OF ANALYSIS FOR C<sub>2</sub>H<sub>2</sub>-O<sub>2</sub> MIXTURES 1:1, WITH 200 SEC DURATION, CORRESPONDING TO 290°C

| Temperature,<br>°C | Mols passed<br>through × 10 <sup>3</sup> |                | Mols formed × 10 <sup>3</sup> |                 |                |   |
|--------------------|--|----------------|-------------------------------|-----------------|----------------|---|
|                    | C <sub>2</sub> H <sub>2</sub>            | O <sub>2</sub> | CO                            | CO <sub>2</sub> | H <sub>2</sub> | HC <sub>2</sub> HOH + HCHO <sup>1</sup> |
| 255                | 8.9                                      | 8.9            | 0.105                         | 0.032           | 0.015          | 0.11                                    |
| 277                | 8.9                                      | 8.9            | 0.30                          | 0.084           | 0.043          | 0.26                                    |
| 297                | 8.9                                      | 8.9            | 1.14                          | 0.37            | 0.108          | 0.84                                    |
| 316                | 8.9                                      | 8.9            | 2.90                          | 0.80            | 0.26           | 1.50                                    |

<sup>1</sup> Computed under the especially founded assumption that the condensable substance consists of formic acid and formaldehyde in the ratio 6:1.

If we had an approximately static speed of reaction, the yield of all substances should remain about the same in the range of small conversions with a doubling of the permeated quantity and simultaneous halving of the duration of the reaction. As can be seen by Table 72, however, this is not the case; rather, the yield decreases with the shortening of the duration of reaction. As an explanation, it can be assumed that the

<sup>1</sup> BODENSTEIN, M., cited p. 380.

<sup>2</sup> KISTIAKOWSKY, G.B., and S. LENHER, *J. Am. Chem. Soc.*, **52**, 3785 (1930).  
LENHER, S., *J. Am. Chem. Soc.*, **53**, 2962 (1931).

<sup>3</sup> STEACIE, E.W.R., and R.D. McDONALD, *J. Chem. Phys.*, **4**, 75 (1936).

<sup>4</sup> BONE, W.A., and ANDREW, *J. Chem. Soc.*, **87**, 1232 (1905).

<sup>5</sup> BRINER and WUNENBURGER, *Helv. Chim. Acta*, **12**, 786 (1929).

reaction produces a period of induction, as can also be observed in other cases.

TABLE 72.—INFLUENCE OF THE REACTION PERIOD ON THE ACETYLENE OXIDATION  
(FROM KISTIAKOWSKY AND LENHER)  
Average Values

| Temperature, °C | Mols passed through $\times 10^3$ |                | Mols formed $\times 10^3$ |                 |                |              | Average duration, sec |
|-----------------|-----------------------------------|----------------|---------------------------|-----------------|----------------|--------------|-----------------------|
|                 | C <sub>2</sub> H <sub>2</sub>     | O <sub>2</sub> | CO                        | CO <sub>2</sub> | H <sub>2</sub> | HCOOH + HCHO |                       |
| 278             | 8.9                               | 8.9            | 0.48                      | 0.088           | 0.073          | 0.51         | 200                   |
| 278             | 17.8                              | 17.8           | 0.18                      | 0.043           | 0.057          | 0.47         | 100                   |
| 278             | 35.6                              | 35.6           | 0.14                      | 0.008           | 0.033          | 0.34         | 50                    |

At 310°, conditions are complicated by the co-effect of the period of induction and a marked decrease in the acetylene concentration during the experiment (on which the speed of reaction is greatly dependent), but they fit into the framework of the rest of the observations. The reaction velocity changes about like the second power of the acetylene concentration and is slightly decreased by oxygen. It thus shows the same characteristics as aldehyde oxidation.

Packing pieces of pyrex into the reaction chamber, so that the free space of about 20 mm was reduced to 1 mm, slowed the reaction considerably. In an experiment at 315°, only 30 per cent of the acetylene reacted in the empty reaction chamber, whereas in the packed vessel only 3 to 4 per cent were converted. Besides, the course of reaction was fundamentally changed, inasmuch as carbon monoxide and water were now the main products of reaction; whereas, in the normal experiments, the condensable substances should be regarded as the primary products. Experiments with a variation of reaction times showed furthermore that the induction time had disappeared.

On the whole it can be concluded: The acetylene-oxidation is apparently a chain reaction in which the wall has a chain breaking effect; in packed vessels one can, moreover, have a catalytic surface reaction; hence it is analogous to the aldehyde oxidation.

Steacie and McDonald<sup>1</sup> later very carefully examined acetylene-oxidation in a static apparatus. The experiments qualitatively confirm in many respects those made by Kistiakowsky and collaborators and give other particulars. In regard to the surface influence the following was established: washing of the pyrex reaction chamber with a NaCl solution caused an acceleration of the reaction, just as with Kistiakowsky and Lenher, but, in contrast to the latter, the results were not well reproducible. On the other hand, experiments in a pyrex vessel washed twice with a saturated KCl solution gave values which are quite reproducible. The ratio CO:CO<sub>2</sub> is practically constant for given relative initial composition, O<sub>2</sub>/C<sub>2</sub>H<sub>2</sub>, and changes but little when the initial composition is varied. Some experimental results are given in Table 73.

<sup>1</sup> Steacie, E. W. R., and R. D. McDonald, *J. chem. Phys.* 4, 75 (1936).

The experiments yield a reaction velocity which is proportional to about the 2.7 power of the acetylene concentration; oxygen has a slightly inhibiting effect but this commonly lies within the limits of experimental error. The temperature coefficient was likewise determined; there was an apparent heat of activation of 33.5 kcal, in good agreement with Spence and Kistiakowsky's value of 34.7 kcal.

TABLE 73.—ACETYLENE OXIDATION AT 320°C, PYREX CONTAINER, COATED WITH KCl, 200 CM<sup>3</sup>. RATIO O<sub>2</sub>:C<sub>2</sub>H<sub>2</sub> = 1 (FROM STEACIE AND McDONALD)

| C <sub>2</sub> H <sub>2</sub> initial,<br>cm Hg | <i>t</i> ,<br>min | CO <sub>2</sub> ,<br>% | C <sub>2</sub> H <sub>2</sub> ,<br>% | O <sub>2</sub> ,<br>% | CO,<br>% | H <sub>2</sub> + N <sub>2</sub> <sup>1</sup> ,<br>% | A <sup>2</sup> | B <sup>3</sup> |
|---|-------------------|------------------------|--------------------------------------|-----------------------|----------|---|----------------|----------------|
| 21.5  | 9.8               | 8.8                    | 31.6                                 | 20.2                  | 37.4     | 2.0   | 4.25           | 1.46           |
| 19.6  | 11.6              | 8.3                    | 32.1                                 | 20.0                  | 37.4     | 2.2   | 4.50           | 1.42           |
| 15.7  | 17.8              | 8.2                    | 31.4                                 | 21.3                  | 37.2     | 1.9   | 4.54           | 1.44           |
| 12.5  | 27.6              | 8.0                    | 31.5                                 | 21.6                  | 37.0     | 1.9   | 4.63           | 1.43           |
| 10.8  | 36.4              | 8.1                    | 31.6                                 | 20.6                  | 37.5     | 2.2   | 4.63           | 1.44           |

<sup>1</sup> The oxygen used contained 1 to 1.4 per cent N<sub>2</sub>.

<sup>2</sup> A = [CO]/[CO<sub>2</sub>].

<sup>3</sup> B = [CO + CO<sub>2</sub>]/[C<sub>2</sub>H<sub>2</sub>] is a measure for the degree of conversion.

Experiments on the influence of the surface in a quartz-packed quartz chamber of 125 cm<sup>3</sup> volume showed the following: At high pressures, the reaction velocity is inhibited by the increase in surface. In the packed chamber at 320°, the reaction order is considerably reduced, approximately to 1.4. The ratio CO:CO<sub>2</sub> is considerably lowered by packing, and in addition it becomes dependent on the pressure in the packed chamber; it drops sharply with decreasing pressure. Obviously the surface reaction, which yields chiefly CO<sub>2</sub>, is of a low order. As a result, its influence is greatest at low pressures and the CO:CO<sub>2</sub> ratio is thus reduced most at those pressures.

That glyoxal and formaldehyde, both of which are formed in the early stage of acetylene oxidation according to Kistiakowsky and Lenher (cited page 401), do not function as intermediary members of a chain reaction is clear from experiments with additions of glyoxal and formaldehyde by Steacie and McDonald. Glyoxal in small quantities does not accelerate acetylene oxidation. In high concentrations, a small acceleration can be noted, but this might be due to the thermal effect connected with the rapid oxidation of glyoxal. Formaldehyde exercises a decidedly inhibiting effect on acetylene oxidation. In an experiment at 320°C with a partial pressure of 9 cm of acetylene, 28.2 per cent of the acetylene had reacted during 44.3 min. With the addition of 5.3 cm of formaldehyde, only about 9.8 per cent reacted under otherwise equal conditions.

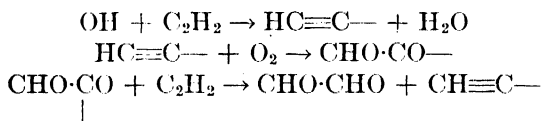
According to the form of the pressure-time curve here observed (at first a small drop in pressure, then a rise), it is reasonable to suppose that an intermediary product is built up in static concentration during the induction period. From the experiments of Steacie<sup>1</sup> and his associates, it is possible to judge how glyoxal, produced as probably the first demonstrable product in acetylene oxidation, can continue to react. At the experi-

<sup>1</sup> HATCHER, HORWOOD, and STEACIE, *J. Chem. Phys.*, **3**, 291, 551 (1935).

mental temperature of 320°, the thermal disintegration of glyoxal is negligible while it continues to oxidize rapidly.

We refer to the original for the individual reactions according to which glyoxal is said to continue to react. Formaldehyde, like glyoxal, also disintegrates only slowly at these temperatures; also however, its oxidation velocity is only small. Spence<sup>1</sup> has pointed out that formaldehyde must be oxidized about 100 times more rapidly than normally in acetylene oxidation. Steacie suggests as an explanation that formaldehyde reacts off by reaction with (intermediarily formed) glyoxal peracid.<sup>2</sup>

Since normal formaldehyde and glyoxal cannot be chain agents, a radical mechanism like the one suggested by Bodenstein is the most probable, even though details must remain unexplained. Lewis and v. Elbe<sup>3</sup> suggest the following mechanism for the formation of glyoxal:



a mechanism against which we can perhaps have no fundamental objections but which of course is likewise not proved.

The Norrish pattern<sup>4</sup> of hydrocarbon oxidation, which employs O-atoms and free radicals, must, according to Steacie, be rejected for acetylene (we shall see that objections can be raised to it also in many other cases), because in it glyoxal and formaldehyde play a role that is excluded according to experiment.

In the presence of nitrogen oxides, acetylene reacts already at considerably lower temperatures (Lenher<sup>5</sup>), between 170° and 250°C, in which trimerous glyoxal is a chief reaction product (up to over 50 per cent of the combined acetylene). In this, NO<sub>2</sub> is probably effective as a homogeneous catalyzer, being reduced to NO, and again forming NO<sub>2</sub> with O<sub>2</sub>, etc., or chains are induced by the reaction NO<sub>2</sub> → NO + O (*cf.* analogous reactions in oxygen-hydrogen combustion, pages 303, 330).

Semenoff<sup>6</sup> points out especially the experiments of Kistiakowsky and Spence,<sup>7</sup> which show the same for acetylene oxidation that Semenoff had demonstrated for aldehyde oxidation in the experiments of Bodenstein,

<sup>1</sup> SPENCE, *J. Chem. Soc.*, 1932, p. 686.

<sup>2</sup> The same result could be obtained by assuming reaction with a corresponding peroxide radical.

<sup>3</sup> LEWIS, B., and G. v. ELBE, "Combustion, Flames and Explosions of Gases," p. 122.

<sup>4</sup> NORRISH, R.G.W., *Proc. Roy. Soc. London, A*, **150**, 36 (1935).

<sup>5</sup> LENHER, S., *J. Am. Chem. Soc.*, **53**, 2962 (1931).

<sup>6</sup> SEMENOFF, "Chemical Kinetics and Chain Reactions."

<sup>7</sup> SPENCE and KISTIAKOWSKY, G.B., *J. Am. Chem. Soc.*, **52**, 4837 (1930).

namely, that, disregarding the induction period, the reaction velocity remains constant over the greater part of the experiment. Kistiakowsky and Spence observed the reaction in a flowing system, causing the gas mixture to circulate by means of a special pump. The condensable products of the gases that left the reaction chamber were drawn off in a trap cooled by means of carbonic acid while the gases were conducted through the reaction chambers again. Conversion was observed by means of pressure changes.

Semenoff is therefore inclined to agree with Spence's view<sup>1</sup> that, in acetylene oxidation, we are dealing, at least in the initial stage, with a nonstatic reaction with chain-branching, the chains probably being induced by the wall since the induction period is shortened by enlarging the wall. Semenoff regards the existence of "critical" diameter found by Spence in the case of acetylene oxidation as the most convincing argument in favor of a degenerate explosion. Spence observes the following: By decreasing the diameter of the chamber from 20 to 6 mm, the reaction velocity decreases to only about 1/3.3 to 1/3.8. With further reduction of the chamber diameter from 6 to 4 mm, the reaction velocity suddenly drops to  $\frac{1}{30}$  of its original value.

That the reaction velocity remains practically constant until almost three-fourths of the acetylene is consumed is actually quite remarkable; for, with a reduction of the initial concentration of the acetylene to one-fourth, the reaction velocity would decrease by more than ten times. Whether Semenoff's explanation of a "degenerate explosion" is correct can be determined only by further experiment. We shall later make the acquaintance of peculiar explosion phenomena, the "cold flames," when we discuss the oxidation of higher hydrocarbons. These phenomena show that nonstatic branched chains progress at quite low temperatures in hydrocarbon oxidation.

*b. The Oxidation of Ethylene.*—The course of ethylene<sup>2</sup> oxidation shows the same characteristics as that of other hydrocarbons: induction period, dependence of the reaction velocity on a higher power of the ethylene concentration, and slight dependence on the oxygen concentration. Packing the reaction chamber retards conversion, a sign that we are dealing with a chain reaction in the gas phase with chain-breaking at the wall. The reaction products appearing in ethylene oxidation have been studied especially carefully by Lenher as well as by Bone, Haffner, and Rance. Lenher studied the reaction by a flow method at atmospheric pressure in a pyrex reaction chamber 20 mm in diameter with a volume of 65 cm<sup>3</sup>. He also carried out experiments by the flow method in larger

<sup>1</sup> SPENCE, *J. Chem. Soc.*, 1932, p. 686.

<sup>2</sup> BONE, W.A., and R.V. WHEELER, *J. Chem. Soc.*, **85**, 1637 (1904). BLAIR and T.S. WHEELER, *J. Soc. Chem. Ind.*, **41**, 303T (1922); **42**, 415T (1923). THOMPSON, H.W., and C.N. HINSHELWOOD, *Proc. Roy. Soc. London, A*, **125**, 277 (1929). LENHER, S., *J. Am. Chem. Soc.*, **53**, 3737, 3752 (1931). SPENCE and TAYLOR, *J. Am. Chem. Soc.*, **52**, 2399 (1930). BONE, HAFFNER, and RANCE, *Proc. Roy. Soc. London, A*, **143**, 16 (1933). STEACIE, E.W.R., and A.C. PLEWES, *Proc. Roy. Soc. London, A*, **146**, 72 (1934).

chambers 55 mm in diameter and 40 cm long; they consisted of pyrex glass, quartz, stainless steel, and aluminum.

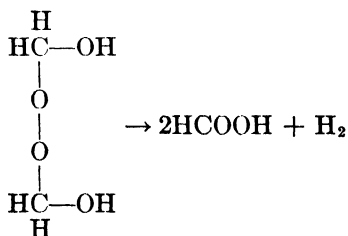
A typical result of analysis for an ethylene-oxygen mixture 1:1, of which 360 cm<sup>3</sup> reacted at atmospheric pressure during 75 sec in the small reaction chamber at 400°, is as follows: 0.1689 gram of condensate, 102.5 cm<sup>3</sup> CO, 11.4 cm<sup>3</sup> CO<sub>2</sub>, and 2.9 cm<sup>3</sup> H<sub>2</sub>. The condensate contained ethylene oxide, ethylene glycol, glyoxal, formaldehyde, formic acid, and water. Thompson and Hinshelwood found the velocity of the ethylene oxidation proportional to the square of the ethylene concentration, and this agrees with the results of Lenher.

If the reaction chamber was packed with pieces of pyrex tubing so that the free distance was reduced from 20 mm to about 1 to 2 mm, the reaction velocity was reduced to an extraordinary degree. In the empty reaction chamber, 70 per cent of the ethylene reacted during 75 sec and at 390°, whereas in the packed container no conversion was proved to be present at 450° and the velocity was measurable only above 500°. The chief reaction products in the packed chamber were CO, CO<sub>2</sub>, and H<sub>2</sub>O, clearly as the result of a surface reaction.

Nitric oxide in small concentrations (3 to 5 per cent) did not accelerate the reaction noticeably at 300° to 400°C. An equimolecular ethylene-nitric oxide mixture yielded CO, CO<sub>2</sub>, and N<sub>2</sub> as gaseous, and glyoxal and formaldehyde as liquid reaction products at 295° and 80 sec of reaction duration.

According to Lenher, of the systems methane,<sup>1</sup> ethylene, and acetylene<sup>2</sup> with nitric oxide, acetylene is the only one that does not combine chemically with nitric oxide.

Experiments were conducted in the larger reaction vessel with a content of 960 cm<sup>3</sup> to analyze more accurately the reaction products that are given in Table 74. The formic acid found was produced by the disintegration of dioxydimethyl peroxide



which decomposes into formic acid with H<sub>2</sub> cleavage.<sup>3</sup> The reaction

<sup>1</sup> SMITH and MILNER, *Ind. Eng. Chem.*, **23**, 375 (1931).

<sup>2</sup> LENHER, S., *J. Am. Chem. Soc.*, **53**, 2962 (1931).

<sup>3</sup> RIECHE, A., "Alkylperoxyde und Ozonide," Theodor Steinkopff, Dresden, 1931.

product, which was condensed out with ice, developed pure hydrogen for days. —

TABLE 74.—OXIDATION OF ETHYLENE ( $85 \text{ C}_2\text{H}_4 + 15\text{O}_2$ ) IN VARIOUS REACTION CHAMBERS WITH A CONTENT OF  $960 \text{ CM}^3$  (FROM LENHER)

| Reaction chamber                                 | % ethylene converted | % of the converted ethylene, which yields the following reaction products |      |                                   |       |
|--|----------------------|---|------|-----------------------------------|-------|
|  |                      | CO, CO <sub>2</sub> , and H <sub>2</sub>                                  | HCHO | (CH <sub>2</sub> ) <sub>2</sub> O | HCOOH |
| Pyrex.....                                       | 9.8                  | 51.2  | 10.2 | 13.7                              | 24.8  |
| Pyrex (3% water vapor in the gases).....         | 9.9                  | 65.0  | 11.6 | 14.7                              | 8.5   |
| Pyrex (3% water vapor in the gases).....         | 9.0                  | 55.5  | 10.8 | 14.4                              | 19.2  |
| Pyrex (KCl-coated)....                           | 9.1                  | 58.0  | 27.7 | 13.5                              | 0.8   |
| Stainless steel.....                             | 4.6                  | 52.0  | 41.8 | 5.1                               | 1.1   |
| Aluminum.....                                    | 5.5                  | 89.8  | 9.6  | —                                 | 0.8   |
| Pyrex, K <sub>2</sub> SiO <sub>3</sub> -coated.. | 5.4                  | 58.6  | 31.7 | 9.7                               | —     |
| Quartz.....                                      | 9.3                  | 57.0  | 27.1 | 11.7                              | 4.3   |

In special experiments, the presence of hydrogen superoxide in the reaction products was demonstrated. The condensate, which was kept in the cold for several days, no longer contained  $\text{H}_2\text{O}_2$ , but it did contain dioxydimethyl peroxide. It was therefore assumed that the latter had formed from hydrogen superoxide and formaldehyde (for the reactions of the peroxides, *cf.* Rieche).

In pyrex containers, dioxydimethyl peroxide is a main reaction product; in quartz containers, only about one-sixth of it is produced; and, in containers that are coated with KCl or  $\text{K}_2\text{SiO}_3$  as well as in aluminum and steel containers, its production is completely suppressed.

It was further shown that ethylene oxide does not noticeably react with oxygen at  $365^\circ$  during 27 sec. Ethylene oxide therefore cannot be an intermediate product of ethylene oxidation.

The oxidation of propylene is completely analogous to that of ethylene. Here too peroxidic substances appear.

Also in ethylene oxidation, the reaction velocity, once the induction period is past, changes remarkably little with the time. Semenoff points out that, in the curves of Thompson and Hinshelwood, this is true of a considerable time interval. In Fig. 192, we reproduce pressure-time curves from Steacie and Plewes that show this perhaps more emphatically. Hinshelwood and Thompson find an apparent heat of activation for ethylene oxidation of 37 to 43 kcal depending on the experimental conditions.



Steacie and Plewes chiefly sought an answer to the question of whether acetaldehyde plays a role as an intermediate product of ethylene oxidation. They used mixtures of  $1(\text{C}_2\text{H}_4 + \text{CH}_3\text{CHO}) + 2\text{O}_2$ . Acetaldehyde alone is almost instantaneously oxidized between  $300^\circ$  and  $350^\circ$ ; at any rate, complete conversion has occurred in 2 min. In mixtures, it is shown that acetaldehyde, as long as its concentration does not reach one-third of that of the ethylene, does not noticeably influence the oxidation of the latter. With higher concentrations of the aldehyde, its accelerating influence at  $430^\circ\text{C}$  makes itself felt. At still higher temperatures, it leads to explosion (e.g., at  $452^\circ$ , 9 cm  $\text{C}_2\text{H}_4$ , and 2.7 cm  $\text{CH}_3\text{CHO}$ ). According to Steacie, it is very likely that, under the conditions in which

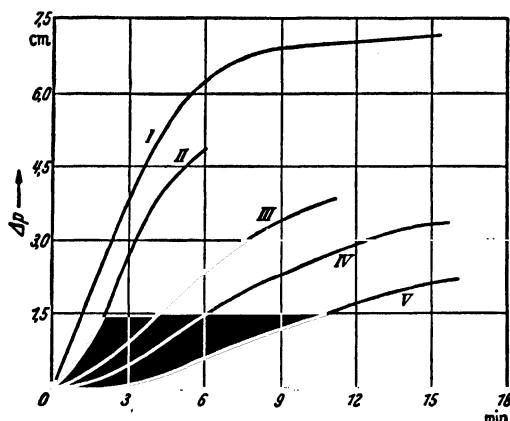


FIG. 192.—Reaction velocity curves (pressure variation as measure) for mixtures of  $\text{C}_2\text{H}_4 + 2\text{O}_2$  at  $452^\circ\text{C}$ . Ethylene initial pressures: 12.4 (I); 10.6 (II); 8.3 (III); 6.8 (IV); and 5.4 cm Hg (V). [From Steacie and Plewes, *Proc. Roy. Soc. London, A*, vol. 146 (1934).]

the aldehyde influence is noticeable, the temperature equilibrium is disturbed simply by its rapid oxidation.

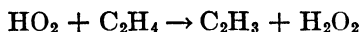
According to Bone, Haffner, and Rance (cited page 405), the induction period of ethylene oxidation is practically suppressed by acetaldehyde, but the main reaction is not noticeably accelerated. This, then, is in agreement with Steacie's results.<sup>1</sup> Steacie concludes that the oxidation of unsaturated hydrocarbons follows a mechanism different from that of the saturated hydrocarbons, since, in contrast to the former, acetaldehyde does not accelerate the reaction. Undoubtedly there is a difference between the groups if only because the double bond furnishes the weakest point for the attack on the molecule; although it should be taken into account, on the other hand, that the double bond has a chain-breaking effect (the recombination of atomic hydrogen is, for example, catalyzed by the unsaturated). That fundamental differences beyond anything

<sup>1</sup> Bone and his associates conclude that an acceleration takes place, but Steacie denies that this follows from their experiments.

caused by the above—as far as the nature of the chain agents is concerned—exist between the saturated and the unsaturated does not yet seem to be proved by the experimental material thus far available.

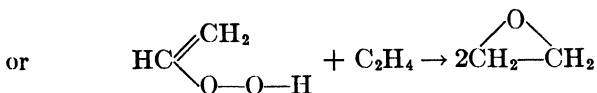
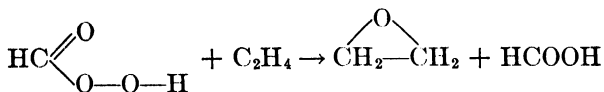
• Ozone accelerates ethylene oxidation considerably. Since the number of oxygen molecules combined in this process exceeds that of the added ozone molecules many times, this finding is a direct confirmation of the presence of a chain reaction.

The question of the mechanism of ethylene oxidation is discussed most extensively by Lewis and v. Elbe.<sup>1</sup> For peroxide formation, they assume a condensation of hydrogen peroxide with formaldehyde<sup>2</sup>—an assumption probably fully supported by Lenher's findings. In this case, the hydrogen superoxide can probably be formed by the reaction of HO<sub>2</sub> with ethylene



HO<sub>2</sub> is quite certainly an intermediary product in oxygen-hydrogen oxidation (page 317). It is therefore reasonable to count on its appearing also during hydrocarbon oxidation. Whether H<sub>2</sub>O<sub>2</sub> is produced by the reaction described or in some other way is not as yet determined.

For the formation of ethylene oxide, Lewis and v. Elbe assume reactions like the following:



Analogous reactions, the conversion of a peracid with an olefin to form olefin oxide and normal acid, are known in solution.<sup>3</sup> It is therefore conceivable that something similar takes place in the gas phase. At any rate, it must not be forgotten that such reactions observed in solutions represent the gross conversion and not necessarily the actual reaction mechanism. Ion reactions could participate especially in the condensed phase. Even though it might therefore be possible that the corresponding conversions take place in the gas phase, it will be necessary to leave

<sup>1</sup> LEWIS and v. ELBE, "Combustion, Flames and Explosions of Gases."

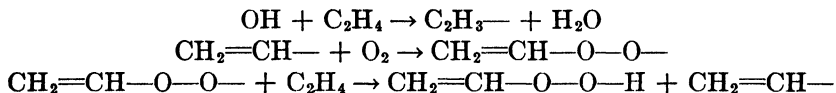
<sup>2</sup> The strong influence of the wall might indicate that the condensation takes place at the wall.

<sup>3</sup> SMITS, *Rec. trav. chim.*, **49**, 675, 691 (1930). BÖESEKEN, *Chem. Weekblad*, **31**, 166 (1934). MILAS and McALVEY, *J. Am. Chem. Soc.*, **55**, 352 (1933). STUURMAN, *Proc. Acad. Sci. Amsterdam*, **38**, 450 (1935).

open for the mechanism the possibility of intermediate steps and eventually even of wall reactions. The same is true for the assumed reactions of the peroxides, which are certain in solution.<sup>1</sup>

The behavior of ethylene in auto-ignition<sup>2</sup> at various pressures will be discussed later in another connection (page 487).

Lewis and v. Elbe attribute the disappearance of the peroxides in containers coated with KCl to destruction of  $\text{H}_2\text{O}_2$  at the wall. As a chain mechanism, we suggest



The appearance of OH-radicals is to be expected for the reasons already given for  $\text{HO}_2$ . However, it is not yet proved.

c. *The Oxidation of Methane.*<sup>3</sup>—The behavior of the paraffins in oxidation, as could be expected, shows few specific differences, except for the first members of the series. For that reason, and also because the lowest paraffins have been especially thoroughly investigated, we shall discuss them individually but shall treat the oxidation of the others collectively.

The oxidation of methane has been widely investigated.<sup>4</sup> General characteristics observed, similar to the reactions already discussed, are the appearance of an induction period and the inhibition of the reaction by packing the reaction chamber. Conversion products are  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , formaldehyde, and, under certain circumstances, like low oxygen concentration and/or high pressure, methanol in more or less high concentrations.

In Fig. 193 is shown the variation in time of the oxidation of methane according to Bone and Gardner. The mixture used is dry  $2\text{CH}_4 + \text{O}_2$  at  $420^\circ\text{C}$ ; the rise in pressure serves as a measure of conversion. Under these conditions, induction periods from several minutes up to over  $\frac{1}{2}$  hr are noted depending on the ratio of surface to volume. The induction period is lengthened by enlarging the surface. The chain-breaking

<sup>1</sup> Cf. in this connection RIECHE, A., cited p. 406.

<sup>2</sup> KANE, G.P., and D.T.A. TOWNEND, *Proc. Roy. Soc. London*, A, **160**, 174 (1937).

<sup>3</sup> Note added to the proofs: Cf. also the recent work of L. Slotin, and D.W.G. Style, *Trans. Faraday Soc.*, **35**, 420 (1939).

<sup>4</sup> BONE, W.A., and J.B. GARDNER, *Proc. Roy. Soc. London*, A, **154**, 297 (1936). BONE and ALLUM, *Proc. Roy. Soc. London*, A, **134**, 586 (1932). NEWITT, D.M., and A.E. HAFNER, *Proc. Roy. Soc. London*, A, **134**, 591 (1932). FORT and C.N. HINSHELWOOD, *Proc. Roy. Soc. London*, A, **129**, 284 (1930). NORRISH, R.G.W., and J. WALLACE, *Proc. Roy. Soc. London*, A, **145**, 307 (1934). NORRISH, *Proc. Roy. Soc. London*, A, **150**, 36 (1935). NORRISH and S.G. FOORD, *Proc. Roy. Soc. London*, A, **157**, 503 (1936). PEASE, R.N., and CHESEBRO, *Proc. Nat. Acad. Sci. U.S.*, **14**, 472 (1928). SACHSSE, H., *Z. physik. Chem.*, Sec. B, **33**, 229 (1936).

influence of the wall thus makes itself preponderantly felt, although under these conditions the reaction chains are rather certainly also induced at the wall. In Table 75, which is likewise taken from Bone and Gardner, the change of the induction time with the temperature is shown, as well as the quantities of formaldehyde formed after  $\frac{1}{3}$ ,  $\frac{2}{3}$ , and  $\frac{3}{3}$  of the induction period has passed.

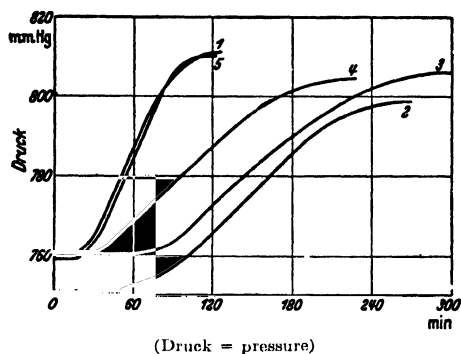


FIG. 193.—Oxidation of  $2\text{CH}_4 + \text{O}_2$  at  $420^\circ\text{C}$  (pressure variation as measure of the reaction velocity. Ratio of surface: volume—1,  $0.8\text{ cm}^{-1}$ ; 2,  $1.2\text{ cm}^{-1}$ ; 3,  $1.6\text{ cm}^{-1}$ ; 4,  $1.2\text{ cm}^{-1}$ ; 5,  $0.8\text{ cm}^{-1}$ . (From Bone and Gardner, *Proc. Roy. Soc. London, A*, vol. 154.)

That formaldehyde is an essential intermediary product of the reaction and that its production during the induction period is responsible

TABLE 75.—INDUCTION PERIODS IN THE OXIDATION OF METHANE, AS WELL AS QUANTITIES OF FORMALDEHYDE FORMED AFTER  $\frac{1}{3}$ ,  $\frac{2}{3}$ , AND  $\frac{3}{3}$  OF THE INDUCTION PERIOD FOR A MIXTURE OF  $2\text{CH}_4 + \text{O}_2$  AT 760 MM Hg INITIAL PRESSURE<sup>1</sup>

| Tempera-<br>ture, °C | Induction<br>period,<br>min | Formaldehyde formed after |               |       |               |       |
|----------------------|-----------------------------|---------------------------|---------------|-------|---------------|-------|
|                      |                             | $\frac{1}{3}$             | $\frac{2}{3}$ |       | $\frac{3}{3}$ |       |
|                      |                             | of the induction period   |               |       |               |       |
|                      |                             | %                         | %             | mm Hg | %             | mm Hg |
| 390                  | 43.5                        | —                         | 0.01          | 0.075 | 0.18          | 1.35  |
| 400                  | 31.5                        | —                         | 0.02          | 0.15  | 0.24          | 1.82  |
| 410                  | 20.5                        | —                         | 0.03          | 0.225 | 0.18          | 1.35  |
| 420                  | 10.5                        | —                         | 0.05          | 0.365 | 0.25          | 1.92  |

<sup>1</sup> Probably 760 mm; pressure not given.

for accelerating the reaction seems extremely likely after what has been said above, especially since formaldehyde, if added intentionally, greatly diminishes the induction time or suppresses it entirely (*cf.* below).

The effect of additions is shown by the following illustrations. Figure 194 shows the influence of methanol in concentrations of 0.25 to 2 per cent (from Bone and Gardner).

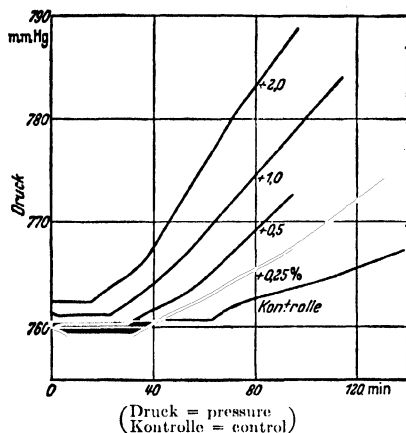


FIG. 194.—Influence of methanol additions on the reaction velocity (pressure variation as a measure) of  $2\text{CH}_4 + \text{O}_2$ , dry, at  $390^\circ$  and  $\sim 760$  mm initial pressure. (From Bone and Gardner, p. 405.)

By means of this addition, the induction time is greatly shortened but not completely suppressed. CO and  $\text{CO}_2$  are, as could be expected, without marked influence. Formaldehyde is greatly effective (Fig. 195). As little as 0.5 per cent suppresses the induction period completely. This is, by the way, a concentration of the same order of magnitude as is found in the reaction of pure methane at the end of the induction period (cf. Table 75). With still higher additions, up to 2 per cent, the reaction is at first further accelerated; 0.25 per cent of formic acid reduces the induction period by one-half; 0.22 per cent  $\text{NO}_2$  shortened it from 50 to 17 min; 0.32 per cent caused it to disappear entirely.

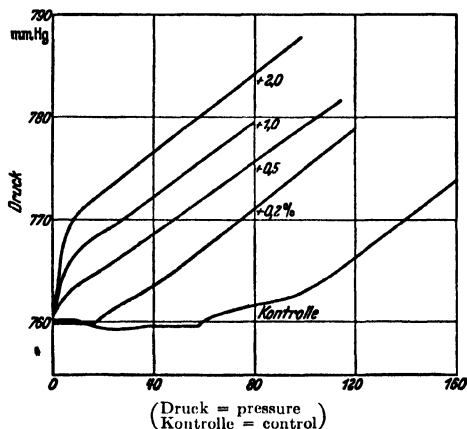


FIG. 195.—Effect of formaldehyde additions on the oxidation of dry  $2\text{CH}_4 + \text{O}_2$  at  $390^\circ\text{C}$ . (From Bone and Gardner, p. 405.)

On the other hand, 0.3 per cent iodine inhibited the reaction so much that, even after 135 min, no rise in pressure was noticeable. This is in agreement with the findings in oxygen-hydrogen reaction (page 303)

and is not unexpected, although it is in contrast to earlier observations by Bone and Allum (cited page 410) with  $2\text{CH}_4 + \text{O}_2$  at  $447^\circ\text{C}$ .

It is conceivable, however, that the effect of the iodine depends considerably on the particular experimental conditions (especially perhaps the condition of the wall).

Peroxides were not found by Bone. Considering the small concentrations in which these compounds are effective, however, a participation of peroxidic materials in the reaction is not absolutely excluded.

In this connection, we shall point out experiments on the oxidation of methanol, likewise made by Bone and Gardner. The reaction—in contrast to methane oxidation—is only slightly dependent on the sur-

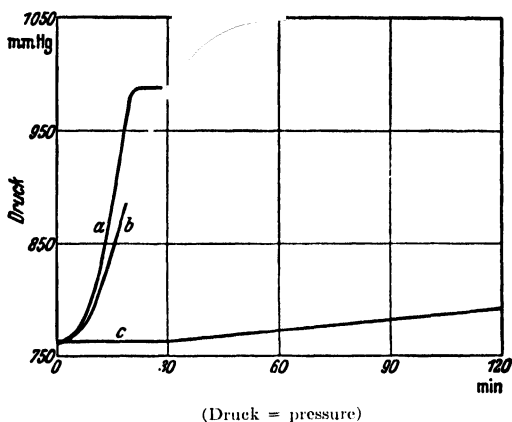


FIG. 196.—Oxidation of methane and of methanol at  $390^\circ\text{C}$  and 760 mm initial pressure. *a*,  $2\text{CH}_3\text{OH} + \text{O}_2$ . *b*,  $\text{CH}_3\text{OH} + \text{O}_2$ . *c*,  $2\text{CN}_4 + \text{O}_2$ . (From Bone and Gardner, p. 405.)

face: volume ratio; the induction period is considerably shorter and the reaction velocity is considerably greater than in the case of methane (Fig. 196). Here, as in all the hydrocarbons, the “richer,” *i.e.*, the mixture richer in fuel, is also the most capable of reaction. As reaction products, the following were proved to be present: formaldehyde, formic acid, occasionally traces of peroxide, preponderantly CO, in smaller quantities  $\text{CO}_2$ , some  $\text{H}_2$ , and of course,  $\text{H}_2\text{O}$ . Methanol combustion is also still considerably accelerated by the addition of formaldehyde.

Formaldehyde itself (*cf.* page 378) is more rapidly oxidized; at  $275^\circ\text{C}$ , the reaction proceeds without an induction period and is noticeably inhibited by an increase in the surface: volume ratio. The half-life period for a mixture of  $2\text{CH}_2\text{O} + \text{O}_2$  at  $275^\circ\text{C}$  and 1 atm, for example, is about 5 to 10 min. The main reaction products are CO and  $\text{H}_2\text{O}$ , also formic acid, peroxides, and per-formic acid. Again, the mixture  $2\text{CH}_2\text{O} + \text{O}_2$  is more capable of reaction than  $\text{CH}_2\text{O} + \text{O}_2$ .

Carbon dioxide, which is proved to be present at low temperatures as a product of methane oxidation, cannot have been produced, as in similar cases, by the oxidation of primarily formed carbon monoxide (because the temperature is too low for that) but must rather have been produced by the oxidation of an intermediary product (*e.g.*, HCHO) or also by the disintegration of such an intermediary product. Perhaps it is also produced in a catalytic wall reaction of the kind we have met in the oxidation of acetaldehyde and propionaldehyde (pages 381, 389).

Methanol is postulated by Bone in his "hydroxylation pattern" as an intermediary product of methane oxidation, and its absence among the normal reaction products is associated with the more rapid oxidizability of methanol (compared with methane). This explanation cannot, however, be correct; for formaldehyde is oxidized considerably more rapidly than methanol and can be isolated as a reaction product nevertheless. Methanol accordingly cannot be an intermediary product of normal methane oxidation. Under certain conditions, methanol can, on the other hand, be obtained in more or less great concentration and must obviously be the product of a conversion that does not belong to the succession of the normal stages of methane oxidation. It is possible to obtain methanol from methane in considerable yields—up to over 50 per cent of the converted methane—and the methane yield will be greater, the greater the pressure (which at the same time permits working at lower experimental temperatures) and the greater the methane:oxygen ratio.<sup>1</sup>

Newitt and Haffner have investigated the oxidation of methane at pressures of 10 to 150 atm and at temperatures between  $\sim 330^\circ$  and  $440^\circ\text{C}$ . The following compilations give a survey of the results. Even at higher initial pressures, the reaction proceeds in a manner similar to that at atmospheric pressure, except that the same reaction velocity is of course obtained at considerably lower temperatures when high pressures are applied. In a mixture of  $8.1\text{CH}_4 + \text{O}_2$  at 106 atm of initial pressure, an induction period of 14 min is observed at  $341^\circ\text{C}$ . In a further reaction period of 22 min, practically all the oxygen is consumed. The available methanol yield rises with increasing initial pressure, but the experiments are not actually comparable, since with rising pressure the temperature was simultaneously reduced; for the aim was always to obtain as high a methanol yield as possible, and, with the duration of the experiment maintained constant, the greater

<sup>1</sup> NEWITT, D.M., and A.E. HAFFNER, *Proc. Roy. Soc. London, A*, **134**, 591 (1932). PICHLER, H., and R. REDER, *Z. angew. Chem.*, **46**, 161 (1933). NEWITT, D.M., *Proc. Roy. Soc. London, A*, **147**, 555 (1934). Cf. also NEWITT, D.M., and D.T.A. TOWNEND, *Combustion Phenomena at High Pressures*, "The Science of Petroleum," Vol. IV, Oxford, 1938.

reaction velocity at higher pressures demands, of course, a lower temperature (Table 76).

TABLE 76.—METHANOL YIELD IN THE REACTION OF  $8.1\text{CH}_4 + \text{O}_2$  AT VARIOUS INITIAL PRESSURES AND TEMPERATURES (FROM NEWITT AND HAFNER)

|                                |     |      |      |      |       |      |
|--------------------------------|-----|------|------|------|-------|------|
| $p_a$ , atm.....               | 10  | 25   | 40   | 48   | 106.4 | 149  |
| Temperature, °C.....           | 400 | 385  | 372  | 373  | 341   | 341  |
| $\text{CH}_3\text{OH}^*$ ..... | 1.1 | 4.8  | 6.1  | 13.7 | 22.3  | 19.0 |
| $\text{HCHO}^*$ .....          | —   | 0.66 | 1.20 | 0.8  | 0.75  | 0.60 |

\* In per cent of combined methane.

In these experiments, the CO content of the gaseous reaction products was extraordinarily small; the ratio  $\text{CO}:\text{CO}_2$  was between 0.06 and 0.35. This is similar to the catalytic oxidation of aldehydes in packed containers.

That considerable methane yields are to be obtained is shown by experiments in a flow system (Table 77), which are conducted at 50 atm

TABLE 77.—METHANE OXIDATION IN A FLOW SYSTEM AT 50 ATM (FROM NEWITT)

| Mixture                                       | Temperature of the reaction, °C | Duration of the reaction, sec | % of the oxidized methane |              |
|---|---------------------------------|-------------------------------|---------------------------|--------------|
|   |                                 |                               | Methanol                  | Formaldehyde |
| $90\text{CH}_4 + 3\text{O}_2 + 7\text{N}_2$ { | 435                             | 5                             | 51                        | 4.1          |
|   | 435                             | 7                             | 49                        | 3.2          |
|   | 425                             | 10                            | 43                        | 3.2          |
|   | 428                             | 20                            | 12                        | 2.2          |

in the neighborhood of  $430^\circ\text{C}$ .<sup>1</sup>

Again it can be seen that a large ratio of methane to oxygen (30:1) as well as short duration is favorable for a high methanol yield. That methanol is produced in a reaction of higher order than formaldehyde seems very probable from Table 78, which the author<sup>2</sup> has compiled from experimental data by Newitt and Haffner.

TABLE 78.—RATIO OF THE ALCOHOL YIELD TO THE ALDEHYDE YIELD IN THE OXIDATION OF METHANE UNDER VARIOUS PRESSURES (FROM NEWITT AND HAFNER)

| Pressure, atm $p$ | $\alpha = \frac{[\text{methanol}]}{[\text{formaldehyde}]}$ | $\frac{\alpha}{p}$ |
|-------------------|--|--------------------|
| 48.2              | 13.0   | 0.27               |
| 106.4             | 31.5   | 0.30               |
| 150               | 41.6   | 0.28               |

<sup>1</sup> NEWITT, D.M., *Proc. Roy. Soc. London, A*, **147**, 555 (1934).

<sup>2</sup> JOST, W., *Z. Elektrochem.*, **41**, 232 (1935).



The ratio of the alcohol yield to that of aldehyde is in these experiments quite exactly proportional to the pressure, as could be expected if the order of the reaction producing methanol were higher by one than that of the reaction that leads to aldehyde formation. The results could

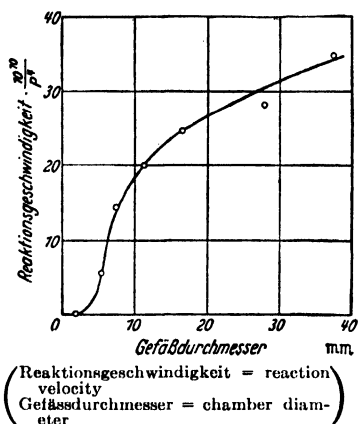


FIG. 197.—Dependence of the oxidation velocity of methane on the chamber diameter. Mixture  $\text{CH}_4 + \text{O}_2$  at  $350^\circ\text{C}$ . (From Norrish and Foord, *Proc. Roy. Soc. London*, A, vol. 157.)

therefore be described most simply if we assumed two reactions competing with one another, of which the one forming methanol and proceeding according to the higher order would be favored by the increasing pressure. Methanol could therefore by no means be an intermediary product of formaldehyde formation. The experiments are to be sure not an absolute proof, since the yields found also depend on the succeeding reactions, but they are nevertheless quite convincing.<sup>1</sup>

Riesenfeld and Gurian<sup>2</sup> were able to isolate formaldehyde, hydrogen peroxide, and ozone even from cooled flames of methane in oxygen. Here formaldehyde and  $\text{H}_2\text{O}_2$  are thought to be produced independently of each other, and ozone

is regarded as a product of the disintegration of  $\text{H}_2\text{O}_2$ .

Methane in mixture with oxygen shows explosion limits at low pressures that are similar to those of hydrogen and carbon monoxide (Neumann and Serbinow<sup>3</sup>). Since hydrogen and carbon monoxide appear as intermediary products in methane oxidation—formaldehyde<sup>4</sup> appearing at low temperatures would, at higher experimental temperatures, disintegrate finally to  $\text{H}_2$  and  $\text{CO}$ —a special investigation would

<sup>1</sup> The observation of Newitt ("The Science of Petroleum," Vol. IV, p. 2885, 1938), that inert dilution materials reduce the reaction velocity and decrease the amount of methanol and formaldehyde that is formed or survives, might be interpreted as conditioned for the most part by the reduction in methane concentration on which aldehyde and alcohol formation are greatly dependent.

<sup>2</sup> RIESENFELD, E.H., and D. GURIAN, *Z. physik. Chem.*, Sec. A, **139**, 195 (1928).

<sup>3</sup> ANDREEV, E.A., and NEUMANN, M.B., *Phys. Z. Sovet.*, **4**, 14 (1933). NEUMANN, M., and A. SERBINOW, *Nature*, **128**, 1040 (1931); *Phys. Z. Sovet.*, **1**, 536 (1932); **4**, 433 (1933). NEUMANN and EGOROW, *Phys. Z. Sovet.*, **1**, 700 (1932). KOWALSKY, A., P. SADOWNIKOW, and N. TSCHIRKOW, *Phys. Z. Sovet.*, **1**, 451 (1932). SADOWNIKOW, P., *Phys. Z. Sovet.*, **4**, 735, 743 (1933). LAWROW, F.A., *Phys. Z. Sovet.*, **4**, 787 (1933).

<sup>4</sup> Probably formaldehyde would disintegrate much more rapidly in reacting mixtures than by itself. In the disintegration of dimethyl ether, for example [FLETCHER, C.J., and G.K. ROLLEFSON, *J. Am. Chem. Soc.*, **58**, 2135 (1936)], formaldehyde that is present is said to disintegrate about fifteen times more rapidly than by itself.

be required to determine in how far the explosion is one only of hydrogen and/or of carbon monoxide. According to Garner,<sup>1</sup> it is quite certain that we are actually dealing here with a carbon monoxide explosion.

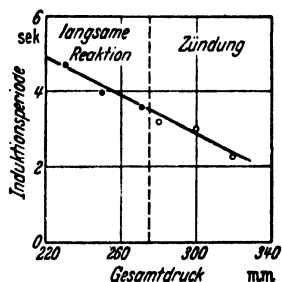
Norrish<sup>2</sup> has likewise investigated methane oxidation more thoroughly. In the neighborhood of 580°C, the reaction between methane and oxygen shows a decided induction period. Upon this follows a rise in pressure which reaches a static maximum velocity

$$w = \frac{dp}{dt} = k[\text{CH}_4]^2[\text{O}_2]p$$

in which  $p$  is the total pressure (addition of nitrogen, for example, favors the reaction).<sup>3</sup>

$k$  depends very much on the condition of the wall. For small chamber diameters, a great dependence on these diameters is an added factor (Fig. 197). Packing the reaction chamber almost totally suppresses the reaction. Ignition is explained by Norrish in this way: In exceeding a certain critical reaction velocity, the thermal equilibrium is disturbed (page 278). Figure 198, in which the induction times for both cases are plotted, shows that no instability appears between the quiet reaction and the one leading to explosion. The "induction period" of the nonexplosive reaction is taken to mean the time up to the turning point on the time-conversion curve, *i.e.*, the time up to the attainment of maximum velocity. These observations are at least in agreement with the suggested explanation for the appearance of explosion. Hydrogen chloride decreases the ignition temperature, and chlorine in low concentrations inhibits the reaction. In higher concentrations, however, it favors reaction.

Iodine effects a decided inhibition in the neighborhood of the ignition temperature. At low temperatures, it has little influence on the velocity of the slow reaction but greatly reduces the induction period. Small quantities of formaldehyde suppress the induction period of the slow reaction but do not change the maximum velocity of the conversion (Fig. 199).



(Reaktionsgeschwindigkeit = reaction velocity  
langsame Reaktion = slow reaction  
Zündung = ignition  
Gesamtdruck = total pressure)

FIG. 198.—Induction periods for the slow reaction and for auto-ignition of  $\text{CH}_4 + \text{O}_2$  at various pressures and 720°C. In the slow reaction the induction period is computed as the time to the attainment of the maximum value of the reaction velocity. (From Norrish, p. 411.)

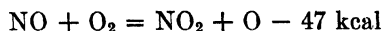
<sup>1</sup> GARNER, W.E., Personal remark. Note added to the proofs: The extensive work has appeared, *Proc. Roy. Soc. London*, A, **170**, 80 (1939).

<sup>2</sup> NORRISH, R.G.W., and S.G. FOORD, *Proc. Roy. Soc. London*, A, **157**, 503 (1936).

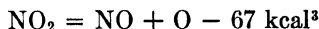
<sup>3</sup> This time law is, by the way, identical to that found by Prettre (p. 310) for oxygen-hydrogen oxidation above the upper explosion limit.

Norrish and Wallace<sup>1</sup> have investigated methane oxidation sensitized by NO<sub>2</sub> (NO<sub>2</sub>, as in oxygen-hydrogen oxidation, has an accelerating effect on the reaction, cf. page 203). In all probability, a reaction chain is induced by oxygen atoms.<sup>2</sup> These O-atoms could, according to

Norrish, be produced by the reaction



or, in spite of the stronger heat absorption, perhaps more probably according to



The formal result derived by Norrish on the basis of an O-atom chain fits remarkably well the discovered dependence on the temperature on the part of the NO<sub>2</sub> pressure that is necessary for ignition.

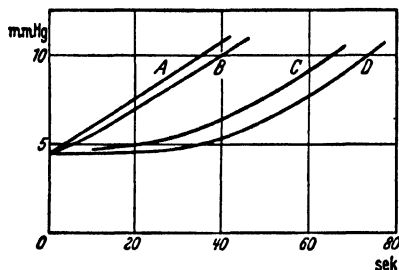
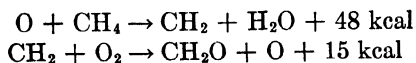
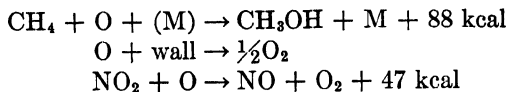


FIG. 199.—Influence of formaldehyde additions on the slow oxidation of CH<sub>4</sub> + O<sub>2</sub> with 200 mm total pressure and 550°C (pressure variation as a measure of conversion). Formaldehyde { A B C D  
5 2 0.5 0 mm Hg.  
(From Norrish, p. 411.)

Norrish's conclusion that, in the presence of NO<sub>2</sub>, reaction chains are induced by oxygen atoms is not improbable. On the other hand, the conclusion that the total methane oxidation, even at low temperatures, is a chain reaction principally continued by oxygen atoms is not so convincing. The pattern is said to be



with chain-breaking according to



With the formal expressions derived from this pattern, a number of observed facts, though not all, can be explained. For details, see the original. There is some evidence for the possibility of an appearance of CH<sub>2</sub>-radicals under certain conditions.<sup>4</sup> We should like to assume,

<sup>1</sup> NORRISH, R.G.W., and J. WALLACE, *Proc. Roy. Soc. London, A*, **145**, 307 (1934). Cf. also NORRISH, *Proc. Roy. Soc. London*, **150**, 36 (1935).

<sup>2</sup> Cf. also NORRISH and J.G.A. GRIFFITHS, *Proc. Roy. Soc. London, A*, **139**, 147 (1933).

<sup>3</sup> SCHUMACHER, H.J., *Z. physik. Chem., Sec. B*, **10**, 7 (1930).

<sup>4</sup> Cf. in this connection BELCHETZ, *Trans. Faraday Soc.*, **30**, 89 (1934). NORRISH, *Trans. Faraday Soc.*, **30**, 103 (1934). Also, the discussion at the spring meeting of the Faraday Society, 1939; in *Trans. Faraday Soc.*, August, 1939.

however, that this pattern, in spite of its simplicity, will have to be modified at least for the range of lower and middle temperatures, both because it cannot explain all the observed facts, and for general reasons that we shall go into when discussing the mechanism of the hydrocarbon oxidation (cf. page 485).

Gimmelmann and Neumann<sup>1</sup> have investigated the oxidation of methane in the presence of methyl nitrite; the reaction mixture was in a quartz container of 30 mm diameter cleansed with hydrofluoric acid; the conversion was observed by means of a recording glass-membrane manometer. For pure methane-oxygen mixtures, they found, in agreement with other works (cf. page 420), the following for the time variations in the rise in pressure:

$$\Delta p = A e^{\Phi t}$$

with

$$\Phi = k p^n e^{-E/RT}$$

where  $n = 2$  and  $E \cong 80,000$  cal.<sup>2</sup>

By the addition of 3 per cent of methyl nitrite in a mixture consisting of  $1\text{CH}_4 + 2\text{O}_2$ , the course of the oxidation is completely changed. The induction period is suppressed, and the reaction itself is greatly accelerated. The mixture of  $\text{CH}_4 + \text{O}_2$  at 64 mm pressure reacts more rapidly in the presence of 3 per cent methyl nitrite at  $418^\circ\text{C}$  than the same mixture reacts without nitrite at  $637^\circ$ . From the experiments, which were carried out with pressures between 26 and 85 mm Hg and between  $418^\circ$  and  $526^\circ\text{C}$ , the reaction velocity at the beginning turned out to be

$$w_0 = k p^n e^{-E/RT}$$

with  $n = 1.7$  and  $E = 16,000$ .

Although wall processes essentially come into consideration for methane oxidation at low temperatures, even in the case of auto-ignition (as well for chain induction as for chain-breaking), the influence of the wall might steadily decrease toward the higher temperatures (Sachsse).<sup>3</sup> Even without the special observations by Sachsse, such a behavior would seem quite probable.

Sachsse determined the induction periods for methane ignition between  $850^\circ$  and  $950^\circ\text{C}$  and found them between  $\sim 10^{-1}$  and  $10^{-2}$  sec. He worked with flow in quartz tubes 12 and 14 mm in diameter which were sometimes packed with quartz tubing. Since a wall influence on ignition could not be determined under these circumstances, Sachsse attempted an explanation of the processes as pure thermal explosion; for this purpose, he used Norrish's pattern. Concerning this, it must be said that

<sup>1</sup> GIMMELMANN, G.A., and M.B. NEUMANN, *Acta Physicochim. URSS*, **7**, 221 (1937). Cf. also GIMMELMANN, G., M. NEUMANN, and P. SOKOV, *Acta Physicochim. URSS*, **5**, 903 (1936).

<sup>2</sup> All such formulas are to be understood to a large extent as interpolation formulas, even though, under special presuppositions (Chap. VIII), they can be theoretically established.

<sup>3</sup> SACHSSE, H., *Z. physik. Chem., Sec. B*, **33**, 229 (1936).

objections that can be made to the special stages of such a mechanism need not necessarily apply to the reaction at high temperatures. In addition, only the following assumptions enter into Sachsse's result: The reaction is induced by the oxygen atoms present in the thermodynamic equilibrium; the reaction of these O-atoms with methane is velocity determining, for which data from the measurements of Harteck and Kopsch<sup>1</sup> have been used (although it is not, of course, certain that atomic reaction observed by Harteck and Kopsch is identical with that postulated by Norrish). According to Harteck and Kopsch, an activation energy of  $\sim 9.5$  kcal is computed from the impact yield at room temperature (of  $10^{-7}$ ), whereas an activation energy of 3 kcal would result from the temperature dependence between  $30^\circ$  and  $189^\circ$ . Sachsse

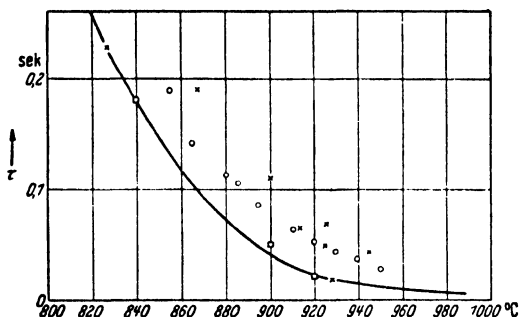


FIG. 200.—Computed (solid curve) and measured values of induction periods in the auto-ignition of methane. Mixture  $62\text{CH}_4 + 38\text{O}_2$  with 670 mm Hg initial pressure. Circles and squares refer to measurements in various reaction chambers. Crosses refer to a chamber packed with quartz tubes. (From Sachsse, p. 414.)

computes with 8 kcal and assumes that the reaction velocity would in this way be correct at  $1100^\circ$  abs to about one power of ten. This can be regarded as a reasonable estimate. Since the heat of dissociation of oxygen amounts to 117 kcal, the concentration of the O-atoms in equilibrium must change with the temperature as  $\exp(-58,500/RT)$ . Added to the resulting temperature dependence, there would also be the heat of activation of the O-atoms amounting to about 8 kcal; and the total heat of activation should therefore amount to about 66.5 kcal. The computation of the induction period with this velocity expression has been undertaken graphically and is essentially equivalent to the computations of Todes (*cf.* page 14) (but carried out independently of Todes). Computed and measured induction periods are shown in Fig. 200; the agreement can be regarded as quite satisfactory. From the temperature dependence of the induction periods, we should compute an apparent activation heat of  $\sim 62$  kcal [that this value does not coincide exactly

<sup>1</sup> HARTECK, P., and U. KOPSCH, *Z. physik. Chem.*, Sec. B, **12**, 327 (1931).

with that valid for the reaction is to be expected; *cf.* the approximation expression (page 18) derived by Todes in which temperature-dependent factors appear in addition to the  $e$  power].

Since, as Sachsse himself emphasizes, the computations remain valid under somewhat more general presuppositions than those in the Norrish pattern, it must probably be assumed that the result will remain essentially correct even though the reaction pattern will have to be modified.

Further data on ignition temperatures of methane-air mixtures of various compositions and pressures will be given later.<sup>1</sup>

TABLE 79.—VALUES OF  $\Phi$  [ACCORDING TO EQS. (3) AND (4)] FOR  $2\text{CH}_4 + \text{O}_2$  AT 770 MM HG (ACCORDING TO EXPERIMENTS BY BONE AND ALLUM COMPUTED BY SEMENOFF)

| Temperature, °C | $1/T \times 10^4$ | $\Phi \text{ min}^{-1}$ | $\Phi \text{ sec}^{-1}$ |
|-----------------|-------------------|-------------------------|-------------------------|
| 447             | 13.89             | 0.30                    | 0.005                   |
| 442             | 13.99             | 0.15                    | 0.0025                  |
| 435             | 14.12             | 0.09                    | 0.0015                  |
| 423             | 14.37             | 0.03                    | 0.0005                  |

Semenoff has applied to the variations in time of methane oxidation the relations that have been derived by him for reactions with chain-branching.<sup>2</sup> The reaction velocity, measured by the rise in pressure, follows this expression up to a conversion of 50 to 60 per cent

$$\Delta p = \text{const } e^{\Phi t} \quad (2)$$

where  $t$  is the time. From Hinshelwood's experiments, he finds

$$\Phi = k[\text{C}^{\text{III}}_2]^{1.5} \quad (4)$$

From the experiments of Bone and Allum (cited page 410), Semenoff determined the  $\Phi$  values according to Table 79.

From this,  $\Phi$  as a temperature function becomes

$$\Phi = Ce^{-46,000/T}$$

with  $C \cong 10^{25}$ . It is difficult to say whether such relations in the case of complicated reactions, in which wall processes take part in an unpredictable manner, mean more than an interpolation formula.

Neumann and Egorov (cited page 416) find the following for the induction period in the explosion of methane-oxygen mixtures as a function of the pressure and the temperature:

$$\tau p^{1.8} e^{-41,000/T} = k \quad (5)$$

<sup>1</sup> TOWNEND, D.T.A., and E.A.C. CHAMBERLAIN, *Proc. Roy. Soc. London, A*, **154**, 95 (1936).

<sup>2</sup> SEMENOFF, "Chemical Kinetics and Chain Reactions"; also *Phys. Z. Sovet.*, **1**, 546, 601 (1932).

The apparent heat of activation (82 kcal) is not very different from that appearing in  $\Phi$  Eq. (4) (92 kcal), just as the pressure dependence is about the same.<sup>1</sup>

*d. The Oxidation of Ethane.*—The oxidation of ethane is similar to that of methane, only at lower temperatures.<sup>2</sup> The reaction shows an induction period which can be greatly reduced by means of various additions (Table 80), among them also iodine (however, *cf.* page 412).

TABLE 80.—THE OXIDATION OF ETHANE AT 316°C AND 720 MM HG (FROM BONE AND HILL)  
Dry Mixture  $C_2H_6 + O_2$

| Mixture + addition      | Induction period,<br>min | Reaction time,<br>min  |
|-------------------------|--------------------------|------------------------|
| $C_2H_6 + O_2$ dry..... | 30                       | 70                     |
| +1% $H_2O$ -vapor.....  | 10                       | 25                     |
| +1% ethanol.....        | 6                        | 18                     |
| +1% iodine.....         | 5                        | 25                     |
| +1% $NO_2$ .....        | 0                        | 20                     |
| +1% formaldehyde.....   | 0                        | 20                     |
| +1% acetaldehyde.....   | 0                        | Instantaneous ignition |

Especially striking is the effect of acetaldehyde, which is in a certain contrast to findings by Steacie and Plewes to be discussed later.

Here too the reaction velocity is greatly dependent on the ethane concentration. Of the mixtures  $C_2H_6 + 3O_2$ ,  $C_2H_6 + 2O_2$ , and  $2C_2H_6 + O_2$ , the last is, at the same pressure and temperature, by far the most capable of reaction (Bone and Hill). Steacie and Plewes find about 3.5 as the apparent reaction order in respect to ethane; their experiments were carried out at an essentially higher temperature (452°) than those of Bone and Hill. As reaction products, besides CO,  $CO_2$ , and  $H_2O$ , aldehydes and, in small amounts, also peroxide are proved to be present (perhaps peracids), as well as ordinary acids. The most careful analyses of the reaction products that appear have been made, again, by Bone and his associates. The results of an experiment carried out at  $304 \pm 1^\circ C$  are shown in Fig. 201. It is noteworthy that the formation of peroxides

<sup>1</sup> Here it is necessary to point out again that, according to Garner, methane explosion is in reality probably a CO explosion (*cf.* p. 416).

<sup>2</sup> BONE, W.A., and S.G. HILL, *Proc. Roy. Soc. London*, A, **129**, 434 (1930). BONE, W.A., and ALLUM, *Proc. Roy. Soc. London*, A, **134**, 578 (1931). STEACIE, E.W.R., and A.C. PLEWES, *Proc. Roy. Soc. London*, A, **146**, 583 (1934). BONE, W.A., and J. DRUGMAN, *Trans. Chem. Soc.*, **89**, 939 (1906). NEWITT, D.M., and A.M. BLOCH, *Proc. Roy. Soc. London*, A, **140**, 426 (1933). SADOWNIKOW, P., *Phys. Z. Sovet.*, **4**, 735, 743 (1933). KOWALSKY, SADOWNIKOW, and TSCHIRKOW, *Phys. Z. Sovet.*, **1**, 451 (1932). TAYLOR, H.A., and RIBLETT, *J. Phys. Chem.*, **35**, 2667 (1931). NEWITT, D.M., *Proc. Roy. Soc. London*, A, **147**, 555 (1934).

and aldehydes runs parallel and that the latter reach their maximum concentration about when the reaction velocity assumes its maximum. Again, under normal conditions, alcohols do not appear in noticeable quantities as reaction products; although, as in methane, considerable yields of alcohol can be obtained under special circumstances. This was first found to be the case by Bone and Drugman concerning ethane under

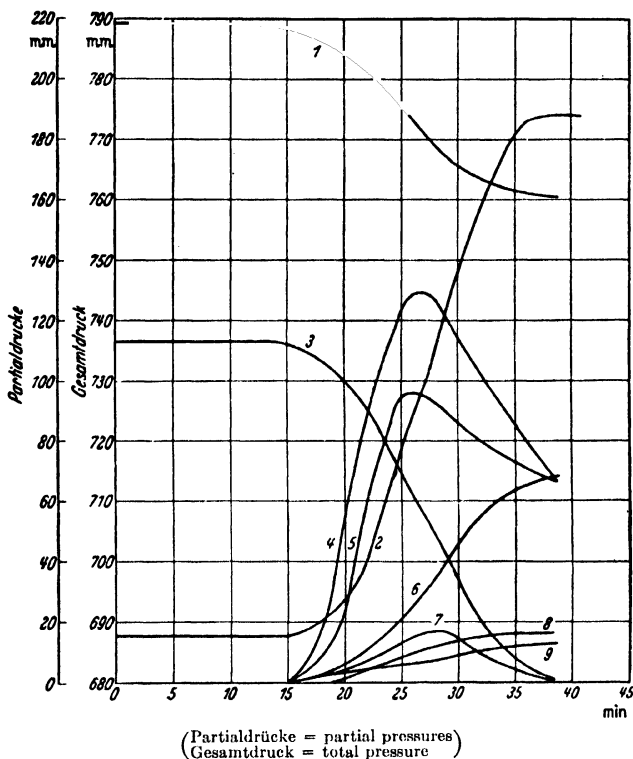


FIG. 201.—Reaction of  $2\text{C}_2\text{H}_6 + \text{O}_2$  at  $304^\circ\text{C}$  and 688 mm initial pressure. Plotted are the total pressure 2, as well as the partial pressures of ethane 1, oxygen 3, total aldehyde (scale  $\times 10$ ) 4; the same for formaldehyde 5, CO 6, peroxide (scale  $\times 10$ ) 7; formic acid (scale  $\times 10$ ) 8,  $\text{CO}_2$  9. (From Bone and Hill, p. 416.)

the influence of ozone at room temperature and at  $100^\circ\text{C}$ . It was also found by Newitt and Bloch at high pressures, analogous to methane. At initial pressures up to 100 atm and temperatures between  $270^\circ$  and  $360^\circ$ , considerable yields of alcohol can be obtained; in one experiment, for example, 60 per cent of the burned ethane. Table 81 gives a survey of the relations.

Information on the reaction velocity can be obtained from Table 82, likewise from Newitt and Bloch.



TABLE 81.—INFLUENCE OF THE INITIAL PRESSURE ON THE SURVIVAL OF THE REACTION PRODUCTS OF A MIXTURE OF  $88.4\text{C}_2\text{H}_6 + 11.6\text{O}_2$  (FROM NEWITT AND BLOCH)

| Initial pressure,<br>atm | Initial temperature,<br>°C | Duration of reaction,<br>min | Percentage of carbon from the burned ethane found in |                        |                         |               |                          |                |                               |
|--------------------------|----------------------------|------------------------------|--|------------------------|-------------------------|---------------|--------------------------|----------------|-------------------------------|
|                          |                            |                              | $\text{C}_2\text{H}_5\text{OH}$                      | $\text{CH}_3\text{OH}$ | $\text{CH}_3\text{CHO}$ | $\text{HCHO}$ | $\text{CH}_3\text{COOH}$ | $\text{HCOOH}$ | Total in condensable products |
| 15                       | 315                        | 3.0                          | 16.0   | 19.4                   | 1.9                     | 4.5           | —                        | —              | 41.8                          |
| 50                       | 294                        | 3.25                         | 17.2   | 14.1                   | 5.2                     | 1.9           | —                        | 0.7            | 39.1                          |
| 75                       | 279                        | 2.5                          | 18.0   | 16.6                   | 6.8                     | 0.4           | 3.6                      | 0.6            | 46.0                          |
| 100                      | 270.5                      | 4.5                          | 23.6   | 14.0                   | 9.7                     | 0.1           | 12.5                     | 0.5            | 50.4                          |

Newitt, in an experiment carried out with a mixture of 90  $\text{C}_2\text{H}_6$ , 30 $\text{O}_2$ , and 7 $\text{N}_2$  at 50 atm and 360°, with a reaction duration of only 4 sec, found the following yields, corresponding to the carbon of the converted ethane:  $\text{C}_2\text{H}_5\text{OH}$ , 62.6 per cent;  $\text{CH}_3\text{CHO}$ , 4.8 per cent;  $\text{CH}_3\text{COOH}$ , 1.1 per cent;  $\text{CH}_4$ , 9.3 per cent;  $\text{CO}$ , 9.2 per cent;  $\text{CO}_2$ , 4.7 per cent.

TABLE 82.—OXIDATION OF ETHANE ( $88\text{C}_2\text{H}_6 + 12\text{O}_2$ ) AT 100 ATM (FROM NEWITT AND BLOCH)

|   |       |     |       |       |      |      |
|---|-------|-----|-------|-------|------|------|
| Temperature, °C.....                          | 262.2 | 265 | 266.5 | 270.5 | 275  | 278  |
| Duration of the induction period,<br>min..... | 25    | 21  | 23.5  | 12    | 5.75 | 4.0  |
| Duration of the reaction period,<br>min.....  | 15    | 13  | 11    | 4.5   | 2.75 | 1.25 |

Also, in ethane oxidation, surface reaction might principally take place during the induction period. Steacie and Plewes found that packing the reaction chamber with quartz tubing shortens the induction period (however, *cf.* page 411 above). Especially when the surface is enlarged six times the induction period is reduced to one-sixth its former value. On the other hand, this enlarging of the surface caused the reaction following the induction period to be greatly suppressed, which points to a chain-breaking at the wall. That the induction period is related to surface processes can be concluded also from experiments by Taylor and Riblett (cited page 422), who worked with pyrex containers between 450° and 480°. Here the induction period amounted to only  $\sim 2$  min and was very irregular. Packing the chamber with pyrex reduced the velocity only a little. After the walls were coated with KCl, the reaction was practically suppressed.

Steacie and Plewes investigated ethane oxidation especially in respect to the role of acetaldehyde as the main intermediary product of conversion. They found that acetaldehyde shortens the induction period, and they are thus in agreement with Bone. With mixtures of  $1\text{C}_2\text{H}_6 + 2.3\text{O}_2$  at  $452^\circ$  and pressures of about 60 to 70 mm Hg, for example, they found induction periods between about 35 and 70 min (the longer the reaction chamber was pumped out after an experiment the longer the induction period in the following experiment, an observation made again and again), which could be reduced to 0.5 up to 1 min by the addition of, to be sure, not too small quantities of acetaldehyde, 14 to 21 mm Hg. That, in spite of a higher temperature in contrast to Bone's observations, no immediate ignition took place with the addition of acetaldehyde might be explained by the fact that Bone worked with mixtures richer in ethane at much higher pressures and that in addition the special condition of the container surface might have played a role (*cf.* page 430). On the other hand, acetaldehyde, according to Steacie and Plewes, is without influence on the main reaction. This might also be due essentially to the reaction conditions changed by the higher temperatures. We shall come back to this later (page 480).

Steacie and Plewes also found ethylene among the reaction products in noticeable concentrations up to 10 per cent, and they conducted special experiments on the oxidation of ethane in mixture with ethylene. These experiments showed that substituting ethylene for ethane made practically no difference during the main reaction. Steacie therefore concludes that ethylene, which is always found as a reaction product, in one case corresponding to 63 per cent of the combined ethane, is an essential intermediary product of the oxidation.

Sadownikow found that, in quartz containers that are treated with hydrofluoric acid, the velocity of the ethane oxidation (for mixtures of  $\text{C}_2\text{H}_6 + 3.5\text{O}_2$ ) is independent of the diameter of the container between the limits of 2 and 40 mm. Since a change in the condition of the wall is of influence on the reaction, however, we can here be dealing only with a special case in which the influence of the diameter of the container does not make itself felt because of the small breaking probability at the wall (in this connection, see Chap. VIII, page 275, as well as Kassel and Storch; also Lewis and v. Elbe, cited page 273).

Ethane also shows an island-like explosion range at low pressure, just as does methane, and here too it must be taken into account (according to Sadownikow, cited page 422) that the explosion is really no ethane explosion but an explosion of the carbon monoxide produced intermediately.

Gimmelmann and Neumann (cited page 416) have also studied ethane oxidation in the presence of methyl nitrite. Without additions, for a mixture of  $\text{C}_2\text{H}_6 + 3.5\text{O}_2$ ,

between 535° and 598°C and with pressures of 96 to 256 mm Hg, they found the time-pressure rise given by

$$\Delta p \cong A e^{\Phi t}$$

with

$$\Phi = \text{const } p^{2.3} e^{-20,400/T}$$

where the apparent heat of activation would thus be 40.8 kcal.

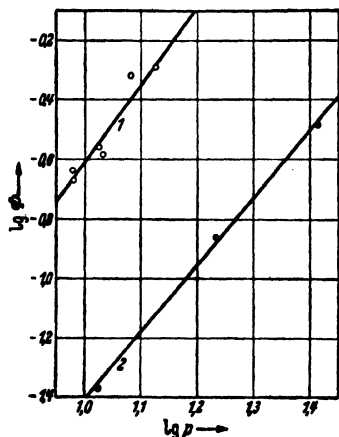


FIG. 202.—Reaction of ethane with oxygen at 597°, 1, and 535°C, 2. For meaning of  $\Phi$ , see the text. (From Gimmelmann and Neumann, p. 413.)

The addition of methyl nitrite again changes the character of the reaction basically (Figs. 202 and 203). The change of the reaction velocity with the concentration of the methyl nitrite under otherwise constant conditions is shown by Fig. 203. If the temperature and pressure are raised, the velocity increases until, at certain critical values, explosion takes place. Even if the reaction is completed in 3 to 10 sec, it is still completely analogous to the slow conversion. Also, in the experiments in which explosion results, the initially constant reaction velocity can still be measured by pressure recordings. Here the reaction velocity follows continuously the velocity that is measured in experiments not leading to explosion (*cf.* Norrish's results in methane oxidation, page 418). The activation energy also remains the same; 37.6 kcal results as a probable activation energy, which to be sure changes greatly with the pressure and composition. It is assumed that heat production is responsible for explosion.<sup>1</sup>

To test the thermal nature of the ignition, experiments were conducted to measure the temperature in the reacting mixture by means of a resistance thermometer. They showed a considerable rise in temperature during the induction period. This rise in

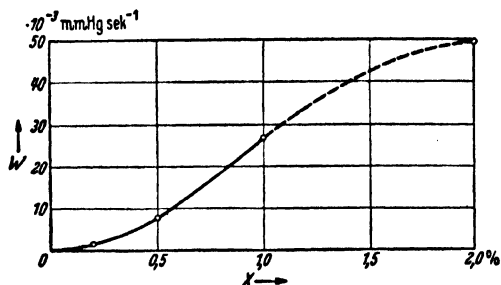


FIG. 203.—Reaction velocity of  $C_2H_6 + 3.5O_2 + X$  per cent methyl nitrite at 408°C and 106 mm Hg initial pressure. (From Gimmelmann and Neumann, p. 413.)

temperature might partly have been conditioned by a catalytic reaction on the surface of the platinum resistance thermometer.

<sup>1</sup> Cf. NORRISH, cited page 417 and GIMMELMANN, G., and P. SOKOV, *Acta Physico-chim. URSS*, 5, 903 (1936).

The formal side of ethane oxidation has been discussed, once more, by Semenoff. The experiments by Bone and Hill can be expressed, up to the moment in which 30 to 40 per cent of the initial substance has reacted, by (change in pressure as a measure of the reaction velocity)

$$\Delta p = Ae^{\Phi t}$$

where

$$\Phi \cong \text{const } p^{2.3} \gamma^3 e^{-19,000/T} = De^{-19,000/T}$$

In this,  $\gamma$  is the share of ethane in the reaction mixture;  $D$  becomes about  $10^{13}$  for  $p = 770$  mm Hg; and  $\gamma = 0.5$ , if  $t$  is figured in minutes. The apparent heat of activation of 38 kcal fits quite well the activation energy of 42 kcal derived in similar experiments by Kowalsky, Sadownikow, and Tschirkov. From the time variations in these experiments, which are carried on at essentially higher temperatures ( $490^\circ$  to  $650^\circ\text{C}$ ) and lower pressures (24 to 70 mm Hg) than those of Bone, there is obtained for  $\Phi$

$$\Phi \cong \text{const } p^{2.2} e^{-21,000/T}$$

again in good agreement. The numerical value of  $\Phi$  depends (as could be expected) greatly on the condition of the wall, as special experiments by Kowalsky have shown.

The strong influence of the surface can, according to Semenoff, be understood from the standpoint of degenerate explosions only by the fact that chain-branching takes place exclusively on the surface. We wish once more to be very reserved regarding any conclusions supported exclusively by formal relations.

*e. The Oxidation of Propane.*—Propane belongs to the materials whose oxidation behavior has been especially thoroughly investigated.<sup>1</sup>

In his first investigation, Pease found the following: In an empty container of pyrex glass, complete reaction was obtained in about 13 sec at  $375^\circ$  with a mixture of  $\text{C}_3\text{H}_8 + \text{O}_2$ . On the other hand, there was hardly a noticeable conversion even at  $500^\circ\text{C}$  in a container packed with glass rods. There was therefore the usual inhibition by the wall, perhaps by chain-breaking. At about  $550^\circ$ , the reaction was again complete. If the walls of the packed chamber were coated with KCl, the temperature at the beginning of a noticeable reaction was raised from  $500^\circ$  to  $575^\circ$ , and even at  $625^\circ$  the reaction was still incomplete.

An investigation of the inhibited reaction in packed containers yielded the following: With KCl coating, there appeared principally, as reaction products in the neighborhood of  $575^\circ$ , unsaturated hydrocarbons, methane, little hydrogen, carbon monoxide, and carbon dioxide. Without KCl coating, at  $550^\circ$ , unsaturated hydrocarbons and methane in addition to larger quantities of CO,  $\text{CO}_2$ , and  $\text{H}_2$  were found. The relative conversion of propane was almost independent of the oxygen concentration. The primary reaction was apparently about of the first

<sup>1</sup> PEASE, R.N., *J. Am. Chem. Soc.*, **51**, 1839 (1929). PEASE and MUNRO, *J. Am. Chem. Soc.*, **56**, 2034 (1934). PEASE, *J. Am. Chem. Soc.*, **57**, 2296 (1935); *Chem. Rev.*, **21**, 279 (1937). HARRIS, E.J., and A. EGERTON, *Chem. Rev.*, **21**, 287 (1937).

order in respect to propane, but, it should be noted, only with the reaction in a packed chamber. If oxygen was displaced by nitrogen, however, only about one-half to one-third as much propane reacted; it was thus not a matter of a purely thermal disintegration of the propane.

In the unpacked but KCl-coated container, the reaction began at  $\sim 325^\circ$ ; as reaction products there were found CO, CO<sub>2</sub>, and at low temperatures little and at high temperatures much unsaturated. At  $300^\circ$ , conversion could not yet be proved, whereas it is considerable at  $325^\circ$ , with a consumption of 30 to 95 per cent of the oxygen. With an increase of the oxygen concentration (mixture 3O<sub>2</sub>:1C<sub>3</sub>H<sub>8</sub>), only about one-half to one-fourth of the oxygen reacts. Thus far, the characteristic phenomena of propane oxidation agree essentially with what we have learned of the lower paraffins and similarly also of aldehydes and unsaturated.

Something entirely new confronts us in propane, something generally noted in all higher normal paraffins and olefins, namely, a range with a "negative temperature coefficient" of the reaction. Pease found the following oxygen consumption by permeation of a mixture of 300 cm<sup>3</sup> oxygen and 100 cm<sup>3</sup> propane:

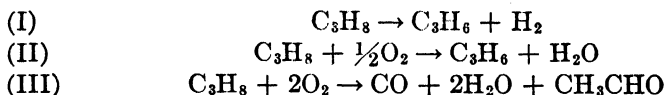
|  |     |     |     |     |     |           |
|--|-----|-----|-----|-----|-----|-----------|
| Temperature, °C.....                     | 325 | 350 | 375 | 400 | 425 | 450       |
| Oxygen consumption, cm <sup>3</sup> .... | 0   | 119 | 115 | 97  | 67  | Explosion |

This course is characteristic—within a very narrow temperature interval, a rise of a nonprovable reaction to the point of considerable conversion, with further rising temperature and a decrease of the conversion until, at a still higher temperature, explosion results. We shall see later that the first sudden rise in velocity, which clearly is to be regarded as explosion, perhaps as degenerate explosion in the sense of Semenoff, namely, as nonstatic reaction which, however, is stopped short at a stage that corresponds to the formation of aldehydes as well as their disintegration products (CO, H<sub>2</sub>O, etc.), is connected with the appearance of "cold flames" (*cf.* page 437) and that these again disappear at higher temperatures, hence the "negative temperature coefficient." The latter, therefore, probably does not refer to a static chemical reaction. Under varied conditions (enriching the mixture, raising the pressure), the cold flame can, by the way, pass over into a regular flaming (*cf.* page 452).

Under the conditions of Pease's experiment, we can substitute nitrogen or other gases for a part of the oxygen at  $375^\circ$  without detriment to the reaction. On the other hand, the reaction is inhibited by this at  $425^\circ$ . If we substitute hydrogen for one-third of the oxygen, no provable

reaction takes place at all.<sup>1</sup> This observation is singular; it is confirmed, however, by later investigations of the higher paraffins (Prettre<sup>2</sup>).

Pease assumed (1929) three types of reactions



which naturally do not describe the actual mechanism.

Butane reveals a behavior in oxidation analogous to that of propane. Later investigations yielded the following details: Peroxides, which are demonstrable in nonpacked reaction chambers without KCl coating, disappear as soon as the wall is coated with KCl without changing essentially the course of the entire reaction. This suggests that stable peroxides either are not formed by the KCl coating or are destroyed but that the unstable intermediary products of reaction, perhaps also of a peroxidic nature, are less influenced by it.

More exact investigation further shows that methanol is among the reaction products and that its formation as well as that of formaldehyde is favored by excess propane; we shall come back to this in discussing Egerton's experiments. Acetaldehyde does not accelerate propane oxidation anywhere near so much as it does ethane oxidation, according to Bone (*cf.* in this connection Steacie's experiments on ethane oxidation, page 425). In order to investigate the slow oxidation of propane in greater detail, Pease lowered the temperature to below 300°; but, since at about 280° the induction period became too long, he added some acetaldehyde in order to shorten it.<sup>3</sup> At this temperature and at a pressure for propane and oxygen of 300 mm each in a noncoated reaction chamber, the induction period (reckoned to a point of time in which the rise in pressure amounted to 1 mm) was found to be 39 min, and the reaction was completed in another 5 min. If, previous to this, 20 mm acetaldehyde was introduced into the reaction chamber, a mild explosion resulted. With 2 mm acetaldehyde, the induction period amounted to 6 min, and the further reaction required a further 5 min (the effect of the acetaldehyde is therefore similar to the aldehyde effect in other cases; *cf.* Norrish's experiments on methane oxidation with additions of formaldehyde, page 418). Under the same conditions, the induction period in a KCl-coated chamber lasted over 5 hr; and, even at 10° lower temperature, 20 mm acetaldehyde caused ignition. With 5 to 10 mm acetaldehyde,

<sup>1</sup> This effect of hydrogen is very peculiar and can perhaps be explained only by a change in the condition of the wall; *cf.* Prettre's observations in oxygen-hydrogen oxidation, Chap. IX, pp. 311ff.

<sup>2</sup> PRETTRE, M., *Compt. rend.*, **203**, 619 (1936); *cf.* also **202**, 954, 1176 (1936); **203**, 561, 1152 (1936); *Ann. Office nat. des combust. liquides*, **11**, 669 (1936).

<sup>3</sup> Ethylene oxide in the place of acetaldehyde was not effective.

the induction period was still 1 to 2 min. Pease assumes—and this assumption seems to agree with all other findings—that the induction period and the effect of the acetaldehyde are connected with surface

TABLE 83.—REACTION OF PROPANE WITH OXYGEN AT 270°C (IN THE PRESENCE OF 5 MM ACETALDEHYDE) IN NONCOATED, EMPTY REACTION CHAMBER [FROM PEASE (PYREX TUBE 2.5 CM IN DIAMETER AND 18 CM IN LENGTH)]

| Mixture                       | Initial pressure, mm Hg |     |     |     |
|-------------------------------|-------------------------|-----|-----|-----|
| C <sub>3</sub> H <sub>8</sub> | 202                     | 211 | 205 | 407 |
| O <sub>2</sub>                | 199                     | 197 | 384 | 203 |
| N <sub>2</sub>                | —                       | 202 | —   | —   |

| Time, min | Rise in pressure, mm Hg |    |     |    |
|-----------|-------------------------|----|-----|----|
| 1         | 0                       | 0  | 0   | 1  |
| 2         | 0                       | 0  | 0   | 2  |
| 3         | 1                       | 1  | 1   | 6  |
| 4         | 2                       | 3  | 2   | 14 |
| 5         | 4                       | 5  | 3   | 28 |
| 6         | 7                       | 9  | 6   | 57 |
| 7         | 12                      | 15 | 10  | 63 |
| 8         | 19                      | 22 | 17  | 64 |
| 9         | 27                      | 30 | 26  | —  |
| 10        | 36                      | 41 | 34  | —  |
| 13        | 60                      | 60 | 63  | —  |
| 25        | —                       | —  | 118 | —  |
| 30        | —                       | —  | 119 | —  |

processes. As a result, it may be assumed that small aldehyde additions will have no influence or only a very small influence on the reaction, if the reaction is permitted to take place under such conditions that the wall can play no role, or at least only a minor one, *e.g.*, in the knocking process in the Otto engine (Chap. XII) or the ignition process in the Diesel engine (Chap. XIII). Such observations, therefore, by no means contradict others made under entirely different conditions in slow oxidation (*cf.* Townend's experiments, pages 476*ff.*).

Pease emphasizes the "all-or-nothing" character of propane oxidation. We have pointed out above in connection with the first rapid rise of the conversion with the temperature and the following "negative temperature coefficient" that we are obviously not dealing with a static reaction at all, but with a kind of explosion.

At first very striking, but according to Lewis and v. Elbe very easy to understand, is the following observation by Pease. In the uncoated reaction chamber, the change of the oxygen concentration as well as the

TABLE 84.—PROPANE OXIDATION IN UNCOATED AND KCL-COATED REACTION CHAMBER AT 270.5°C WITH 5 MM ACETALDEHYDE (FROM PEASE)

| Initial pressure,<br>mm Hg    |                | Time, during which the rise in<br>pressure went from 20 to 40 mm |                  |
|-------------------------------|----------------|--|------------------|
| C <sub>3</sub> H <sub>8</sub> | O <sub>2</sub> | Without KCl coating  | With KCl coating |
| 400                           | 200            | 1  | 3                |
| 200                           | 400            | 2  | 22               |

TABLE 85.—OXIDATION OF PROPANE, AS ABOVE, BUT IN KCL-COATED PYREX CHAMBER AT 280°C WITH THE ADDITION OF 10 MM ACETALDEHYDE (THE LAST EXPERIMENT DESIGNATED WITH \* WITH THE ADDITION OF 5 MM ALDEHYDE) (FROM PEASE)

| Mixture                       | Initial pressure, mm Hg |     |     |     |     |
|-------------------------------|-------------------------|-----|-----|-----|-----|
| C <sub>3</sub> H <sub>8</sub> | 195                     | 215 | 213 | 408 | 295 |
| O <sub>2</sub>                | 196                     | 198 | 403 | 204 | 289 |
| N <sub>2</sub>                | —                       | 204 | —   | —   | —   |

| Time, min | Rise in pressure, mm Hg |    |     |    |    |
|-----------|-------------------------|----|-----|----|----|
| 1         | 0                       | 1  | 0   | 1  | 0  |
| 2         | 0                       | 4  | 1   | 4  | 0  |
| 3         | 1                       | 5  | 1   | 12 | 1  |
| 4         | 2                       | 6  | 1   | 26 | 1  |
| 5         | 2                       | 8  | 1   | 49 | 1  |
| 6         | 3                       | 10 | 1   | 56 | 2  |
| 7         | 3                       | 13 | 1   | 57 | 2  |
| 8         | 3                       | 15 | 1   | —  | 3  |
| 9         | 4                       | 18 | 2   | —  | 4  |
| 10        | 4                       | 22 | 2   | —  | 5  |
| 12        | 5                       | 30 | 3   | —  | 10 |
| 14        | 6                       | 40 | 3   | —  | 19 |
| 16        | 7                       | 50 | 4   | —  | 36 |
| 18        | 7                       | 59 | 5   | —  | 63 |
| 20        | 8                       | 60 | 6   | —  | 87 |
| 30        | 14                      | —  | 10  | —  | 87 |
| 40        | 20                      | —  | 17  | —  | —  |
| 50        | 27                      | —  | 34  | —  | —  |
| 60        | 38                      | —  | 63  | —  | —  |
| 70        | 49                      | —  | 90  | —  | —  |
| 80        | 56                      | —  | 103 | —  | —  |
| 90        | 57                      | —  | 112 | —  | —  |



addition of nitrogen is practically without influence on the reaction (Table 83). The reaction velocity and the induction period are according to this practically independent of the oxygen pressure and the addition of nitrogen but are very dependent on the propane concentration, analogous to other cases.

The picture changes if we observe the conversion in the same chamber but after coating the walls with KCl (by filling the chamber with a KCl solution, permitting it to stand for some time, draining it carefully, and then drying; the remaining KCl coating is not visible and can be recognized only in the behavior of the reaction). The induction period rose at 280° and from 40 min to over 5 hr. Aldehyde additions reduced the induction period, but the following reaction was still retarded (Table 84).

In Table 85 from Pease, we present experiments that were carried out with and without nitrogen additions in a KCl-coated chamber. In order to compensate for the deceleration of the reaction by KCl, he had, as opposed to earlier experiments, raised the temperature from 270° to 280°, and likewise (except in one experiment) he had increased the aldehyde addition from 5 to 10 mm. In these experiments, the reaction is greatly accelerated by nitrogen addition; the same is effected by oxygen but with the difference that nitrogen additions also shorten the induction period, whereas an increase of the oxygen concentration accelerates the reaction only after the completion of the induction period.

There is little reason to doubt the correctness of the explanation given by Lewis and v. Elbe<sup>1</sup> for this behavior. With a great probability of chain-breaking at the wall, as could be assumed with KCl coating, the velocity of the diffusion of chain agents to the wall is determining for the breaking, which on its part depends on foreign gas additions, hence the sensitivity to nitrogen additions and the dependence of the reaction velocity on oxygen partial pressure. With small breaking probability at the wall, as is obviously the case without KCl, the diffusion to the wall is no longer velocity determining, since a practically uniform concentration of the chain agents exists constantly in the entire chamber; as a result, the addition of foreign gas cannot influence the reaction. The difference in the behavior of oxygen and nitrogen during the induction period must rest on the fact that oxygen, in contrast to nitrogen, actively takes part in the reaction occurring during this time and perhaps changes the condition of the surface in a manner about which we can as yet make no assertions.<sup>2</sup>

Egerton and Harris<sup>3</sup> have investigated propane oxidation in detail

<sup>1</sup> LEWIS, B., and G. v. ELBE, *Chem. Rev.*, **21**, 285 (1937). Cf. also Chap. VIII, pp. 273ff.

<sup>2</sup> Cf. Prettre's observations with oxygen-hydrogen, pp. 310ff.

<sup>3</sup> HARRIS, E.J., and A. EGERTON, *Chem. Rev.*, **21**, 287 (1937).

under varied conditions, laying special stress on a careful analysis of the reaction products. The experiments were carried out partly in a flow system (reaction chamber 10 cm long, 1.1 cm inner diameter) and partly in a static apparatus (quartz reaction chamber 42 cm long, 1.4 cm inner diameter).

Experiments according to the static method in a reaction chamber washed with hydrofluoric acid as well as after washing of the chamber with KCl and NaCl solutions are shown by Table 86. The data refer to TABLE 86.—OXIDATION OF 1  $C_3H_8 + 1O_2$  AT 1 ATM, ACCORDING TO A STATIC METHOD (FROM HARRIS AND EGERTON<sup>1</sup>)

| Chamber                                       | Tem-<br>pera-<br>ture, °C | Con-<br>sumed                 |                | Formed          |      |                                |                |                 |      |      |                    |   |                  |
|---|---------------------------|-------------------------------|----------------|-----------------|------|--------------------------------|----------------|-----------------|------|------|--------------------|---|------------------|
|   |                           | Mols × 10 <sup>4</sup>        |                |                 |      |                                |                |                 |      |      |                    |   |                  |
|   |                           | C <sub>3</sub> H <sub>8</sub> | O <sub>2</sub> | CO <sub>2</sub> | CO   | C <sub>n</sub> H <sub>2n</sub> | H <sub>2</sub> | CH <sub>4</sub> | HCHO | RCHO | CH <sub>3</sub> OH | C <sub>2</sub> H <sub>5</sub> OH <sup>a</sup> | H <sub>2</sub> O |
| Quartz (cleaned).....                         | 322                       | 25                            | 47.4           | 5.3             | 28.2 | 2.8                            | 0.8            | 6.9             | 3.7  | 2.0  | 8.0                | 0   | 41               |
| Quartz (KCl).....                             | 351                       | 21.8                          | 43.9           | 5.5             | 23   | 4                              | 0.7            | 4               | 2.6  | 3.4  | 6.4                | 0   | 40.5             |
| Quartz (KCl).....                             | 337                       | 22.8                          | 46             | 7.8             | 25.2 | 4.6                            | 0.6            | 4.4             | 2.8  | 3.2  | 6.7                | 0   | 39               |
| Quartz (NaCl).....                            | 323-338                   | 24.8                          | 45.7           | 7.7             | 19.6 | 3.6                            | 1.4            | 6.4             | 4.1  | 0.7  | 3.6                | 1.8   | 46               |
| Quartz (NaCl).....                            | 351                       | 23.1                          | 42.3           | 6.0             | 22.6 | 5.3                            | 0.3            | 3.4             | 2.8  | 2.4  | 1.6                | 1.6   | 39               |
| Quartz (NaCl).....                            | 351                       | 23.1                          | 42.5           | 5.7             | 21.4 | 4.6                            | 0.9            | 4.9             | 2.5  | 2.9  | 3.1                | 10.8  | 41               |
| Quartz (Fe <sub>2</sub> O <sub>3</sub> )..... | 355                       | 16.4                          | 28.4           | 8.9             | 10.7 | 1.3                            | 0.3            | 4.0             | 0    | 2.3  | 0                  | 0   | 25               |
| Graphite tube.....                            | 320                       | 6.7                           | 20.5           | 11.5            | 5.2  | 0.6                            | 1.0            | 3.9             | 0    | 2.5  | 1.6                | 0   | 9                |

<sup>1</sup> For methods of analysis, see E.J. Harris, *Analyst*, **62**, 729 (1937).

<sup>2</sup> Chiefly ethylene and propylene.

<sup>3</sup> Small quantities of higher alcohols are contained in it.

a reaction that has completely run its course; data on the duration of the reaction are lacking. As has been repeatedly mentioned in other cases, the duration of the induction period decreased when the same reaction chamber was used several times.

The chief reaction products are CO and  $H_2O$ , but, in addition, hardly negligible quantities of unsaturated, of aldehydes, and also of alcohol, chiefly methanol, appear; further, as in all experiments of that nature,  $CO_2$ , and again, in agreement with other findings, relatively more  $CO_2$  at low experimental temperatures where the presuppositions for a catalytic surface oxidation probably of aldehydes are given. Aldehydes and alcohol are all present in comparable concentrations.

Flow experiments yielded analogous results, showing, in agreement, by the way, with many other findings,<sup>1</sup> that a variation in the duration

<sup>1</sup> Cf. especially JOST, W., L. v. MÜFFLING and W. ROHRMANN, *Z. Elektrochem.*, **42**, 488 (1936).

of the experiment had very little influence if any induction time, as well as the normal reaction time, had passed, again a confirmation of the assumption that we are dealing by no means with a static reaction.

The peroxides observed in Pease's flow experiments were not present in the static experiments; they were, however, obtained in flow experiments in a quartz chamber washed with acid. The peroxide yield is very sensitive to the poisoning of the wall. After several successive experiments in the same chamber, the peroxide yield decreases, although it can again be increased by cleaning the surface with acid. In soda-glass tubes, no peroxide is formed; pyrex (as in Pease's experiments) acts like quartz. If hot, gaseous reaction products are conducted through soda-glass tubes, the peroxides are momentarily destroyed; hence no peroxides were found in the static experiments, although they can be proved to be present if the entire reaction chamber is dipped in cold water before the reaction products are removed.<sup>1</sup>

An analysis of the condensed reaction products from flow experiments resulted in the following: The condensate was distilled at 22 mm pressure, and the distillate consisted chiefly of methanol. The peroxides disintegrated during the distillation. In the first experiment, the peroxide estimated as  $\text{H}_2\text{O}_2$  comprised about 10 per cent of the entire liquid before distillation; with fast distillation, violent explosion took place (Table 87).

A greater part of the peroxides does not consist, according to the experimental results, of those which form acids during disintegration. The dioxydimethyl peroxide ( $\text{CH}_2(\text{OH})\text{—O—O—CH}_2\text{—OH}$ ) obtained by Lenher (*cf.* page 406) in ethylene oxidation was doubtless present. The ratio of formaldehyde to hydrogen superoxide in the first experiment

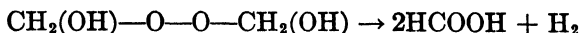
TABLE 87.—ANALYSIS OF 1 GRAM LIQUID REACTION PRODUCTS OF PROPANE OXIDATION (FROM HARRIS AND EGERTON)

| Products                                 | Experiment No. 1 | Experiment No. 2 <sup>1</sup>           |  |
|--|------------------|---|--|
|  | Residue at 40°C  | Distillate, $\frac{1}{3}$ of the volume | Residue, $\frac{2}{3}$ of the volume at 54°C |
| $\text{CH}_3\text{OH}$ .....             | Trace            | 0.300                                   | Trace  |
| $\text{HCHO}$ .....                      | 0.309            | 0.016                                   | 0.045  |
| $\text{CH}_3\text{CHO}$ .....            | ?                | 0.076                                   | 0.085  |
| Peroxide as $\text{H}_2\text{O}_2$ ..... | 0.180            | 0.004                                   | 0.022  |
| Total.....                               | 0.489            | 0.396                                   | 0.193  |
| $\text{H}_2\text{O}$ .....               | 0.511            | 0.604                                   | 0.807  |

<sup>1</sup> Small quantities of acid are not included in the table.

<sup>1</sup> All these observations are also of special importance in judging the experiments of other authors.

was 2:1, corresponding to this peroxide. Disintegration of the peroxide condensate with alkali furnished a gas that consisted of 80 per cent hydrogen and 20 per cent oxygen, the hydrogen corresponding to the equation



This peroxide, which is noticeably dissociated at room temperature, probably does not exist in the gas phase. Egerton ascribes this to the fact that the hydrogen content of the gases is not increased when the gases are conducted through a soda-glass tube that disintegrates the peroxides. Probably  $\text{H}_2\text{O}_2$  and acetolyl peroxide are formed in the gas phase.

Iron oxide apparently favors the surface reactions.

Special experiments showed that the yield of other reaction products does not depend on the quantity of the peroxides present. The influence of the surface is difficult to prove exactly in static experiments, because the surface itself changes in the course of the experiment. Table 88 shows the results of static experiments (1 atm initial pressure) in which samples were taken at predetermined pressures.

From this it follows that (1) the quantities of oxygen and propane consumed are about in the ratio of 2:1, just as in Pease's analogous experiments; (2) carbon monoxide, carbon dioxide, and methanol constantly increase, probably as a result of the disintegration of the products of chain reaction; (3) the water, hydrogen, and aldehyde formed are proportional to the degree of conversion and are therefore probable products of chain reactions; (4) propylene and methane appear to be formed early in the reaction; and (5) the ratio of water formed to oxygen consumed is 1:1.

TABLE 88.—ANALYSIS OF REACTION PRODUCTS OF PROPANE OXIDATION, MIXTURE  $1\text{C}_3\text{H}_8:1\text{O}_2$  AT 1 ATM INITIAL PRESSURE (FROM HARRIS AND EGERTON)

| Gases consumed, mols $\times 10^4$ |              | Reaction products, mols $\times 10^4$ per $10^{-3}$ mol consumed $\text{C}_3\text{H}_8$ |               |             |                        |              |               |               |               |                        |                      | Temperature, $^{\circ}\text{C}$ |
|------------------------------------|--------------|---|---------------|-------------|------------------------|--------------|---------------|---------------|---------------|------------------------|----------------------|---------------------------------|
| $\text{C}_3\text{H}_8$             | $\text{O}_2$ | $\text{O}_2$ consumed   | $\text{CO}_2$ | $\text{CO}$ | $\text{C}_2\text{H}_6$ | $\text{H}_2$ | $\text{CH}_4$ | $\text{HCHO}$ | $\text{RCHO}$ | $\text{CH}_3\text{OH}$ | $\text{H}_2\text{O}$ |                                 |
| 8.1                                | 13.3         | 16.4  | 1.0           | 5.3         | 2.7                    | 0.6          | 5.7           | 0.7           | 1.0           | 0.8                    | 17.9                 | 320                             |
| 14.2                               | 24.0         | 16.9  | 1.55          | 8.4         | 1.76                   | 0.3          | 5.3           | 1.4           | 1.1           | 2.4                    | 17.4                 | 325                             |
| 22.4                               | 39.8         | 17.8  | 1.34          | 9.4         | 1.83                   | 0.3          | 1.1           | 0.9           | 1.2           | 2.0                    | 17.4                 | 340                             |
| 25.0                               | 47.4         | 18.9  | 2.1           | 11.3        | 1.1                    | 0.3          | 2.7           | 1.5           | 0.8           | 3.2                    | 16.8                 | 322                             |
| 25.7 <sup>1</sup>                  | 50.2         | 19.5  | 2.3           | 9.7         | 0.7                    | 0.3          | 2.6           | 1.2           | 0.6           | 2.7                    | 18.2                 | 307                             |

<sup>1</sup> Traces of acetaldehyde contribute to the shortening of the induction period.

Special analyses showed that the degree of conversion and the rise in pressure are not proportional to one another, probably as the result of the disintegration of the reaction products. This is not surprising in itself, but it probably is not taken into account and must also be considered in evaluating other experiments.

The addition of individual reaction products to the initial mixture in the ratio 1:1 at 300° to 340°C resulted in the following: Formaldehyde lengthened the induction period,<sup>1</sup> and acetaldehyde shortened the induction period considerably and increased the methanol yield. Propylene reduced the induction period; methanol was without influence.

The amount of propylene formed in the reaction products is quite independent of the original propane:oxygen ratio as well as of the initial addition of propylene. The fact that the relative quantity of propylene in an earlier stage of reaction is greater and not dependent on the propane concentration seems to suggest that its formation is connected with products that induce the reaction—perhaps beginning with aldehydes—and not with the direct reaction of the propane.

Pease<sup>2</sup> has recently investigated the “negative temperature coefficient” in propane oxidation, which he first observed. He had found that the reaction velocity of propane oxidation at 270°, below the limit for cold flames, in an uncoated pyrex container was independent of the oxygen concentration and proportional to about the first to the second power of the propane concentration. Newitt found that, above the limit for cold flames but below the true ignition point, the equimolecular mixture is the most capable of reaction (at 360 mm Hg and 408°C), *i.e.*, the reaction velocity is about proportional to the product of O<sub>2</sub> and the propane concentration. Pease repeated Newitt’s experiments in a somewhat modified form in a pyrex container cleaned with HNO<sub>3</sub> and H<sub>2</sub>O at 400°. He finds the velocity dependent on both O<sub>2</sub> and the propane concentration, proportional probably to a higher power than the first. This suggests two different reaction mechanisms above and below the “cold-flame” range.

A series of further experiments were made at 10° intervals between 300° and 430° in which, according to Newitt’s results, the cold-flame range was crossed about between 290° and 320°. Since Newitt used a container with a diameter of 5.5 cm, however, and Pease used one with a diameter of 2.0 cm, Newitt might have been just outside the cold-flame

<sup>1</sup> Considering our repeated statement that the “all-or-nothing” reaction of propane oxidation (as well as the analogous cold-flame processes in higher paraffins, naphthalenes, etc.) is to be understood as an explosion that is stopped short at the stage of the aldehyde and its disintegration products, the inhibiting effect of formaldehyde here proved is perhaps not without interest.

<sup>2</sup> PEASE, R.N., *J. Am. Chem. Soc.*, **60**, 2244 (1938). Cf. in this connection NEWITT, D.M., and his associates, *J. Chem. Soc.*, 1937, pp. 1656, 1665, 1669.

range. In the pressure recordings, no indications of cold flames were found. Extrapolated curves yield an activation energy of  $\sim 29$  kcal for the lower range and about 38 kcal for the upper.

**5. The Slow Oxidation of Further Hydrocarbon Compounds. Cold Flames.**<sup>1</sup> *a. The Works of Prettre.*—Prettre<sup>2</sup> was the first to study in detail the luminous phenomena and ignition ranges connected with the slow oxidation of paraffins, olefins, naphthalenes, alcohols, aldehydes, and ethers. As we shall see, these phenomena (which we have already encountered, pages 388, 428) might be caused by the same chemical reactions that are responsible for the knocking process in engines. After the presence of cold flames in the engine itself was successfully demonstrated, the connection might be regarded as proved.<sup>3</sup>

The appearance of luminescence as well as of "cold flames" in fuel vapor-air mixtures was first discovered by Perkin<sup>4</sup> in hydrocarbons, ethers, fatty acids (also, carbon disulphide) at temperatures of about 200° to 250°C upward. In this oxidation, connected with light emission, no rapid rise in temperature as in normal combustion appears, even though, as we shall see later (page 445), a certain rise in temperature (of the order of magnitude 100°C) is connected with the appearance of the cold flame, and even though the cold flame under certain conditions can pass over into a regular ignition.

Luminescence phenomena in oxidation can, according to Prettre, be obtained with almost all fuels (except H<sub>2</sub>). To be sure, methane, carbon monoxide, and benzol hydrocarbons display this phenomenon only in a narrow temperature interval (of the order of magnitude of several 10°C) under the regular ignition temperature as well as during the induction period preceding ignition.

In order to observe the luminescence, Prettre conducted the dried fuel vapor-air mixture with a known flow velocity (between about 0.3 and 6 liters/hr) through a reaction chamber of pyrex glass or quartz (depending on the experimental temperature) with 5.4 cm inner diameter

<sup>1</sup> Cf. in this connection the addresses at the anniversary of the Bach-Engler Autoxidation Theory, *Acta Physicochim. URSS* (3/4), **9**, (1938), which cannot be treated here.

<sup>2</sup> PRETTRE, M., *Ann. Office nat. des combust. liquides*, **6**, 7, 269, 533 (1931); **7**, 699 (1932); **11**, 669 (1936); *Bull. soc. chim.*, (4), **51**, 1132 (1932). Cf. further PRETTRE, M., "The Science of Petroleum," Vol. IV, pp. 2950ff., Oxford, 1938.

<sup>3</sup> PELETIER, L.A., S.G. VAN HOOGBSTRATEN, J. SMITTENBERG, and P.L. KOOYMAN, *Chaleur et ind.*, January, 1939.

<sup>4</sup> PERKIN, W.H., *J. Chem. Soc.*, **41**, 363 (1882). Similar observations are made by G.S. TURPIN, *Brit. Assoc. Advancement Sci. Rept.*, **75**, 776 (1890). DIXON, H.B., *J. Chem. Soc.*, **75**, 600 (1899); *Rec. trav. chim.*, **46**, 305 (1925). SMITHELLS, *Brit. Assoc. Advancement Sci. Rept.*, 1907, p. 469. GILL, F., E.W. MARDELS, and H.C. TETT, *Trans. Faraday Soc.*, **24**, 574 (1928).

and 10 cm length, with entrance and exit pipes  $1\frac{1}{2}$  mm wide, which was heated in an electric oven with a lateral window.

If a pentane-air mixture with an excess of air is conducted through the reaction chamber by heating the latter slowly, a feeble light-blue luminescence becomes visible in the darkened room at about  $240^{\circ}$ , the intensity of which rapidly rises up to  $300^{\circ}$  to  $330^{\circ}$  and then remains constant. From about  $525^{\circ}$  to  $550^{\circ}$  on, the luminescence can no longer be distinguished, owing to the glow of the walls. Ignition appears only at  $660^{\circ}$  to  $670^{\circ}$ , with a blue flame similar to that of carbon monoxide.<sup>1</sup> Here the flame is extinguished and ignites about every  $\frac{1}{2}$  sec. Probably we are here dealing essentially with the combustion of CO (and possibly  $H_2$ ), since the pre-reaction has led to these products.

The temperature at which luminescence appears here lies in the neighborhood of those at which Lewis<sup>2</sup> and Mondain-Monval<sup>3</sup> had, by heating pentane-air mixtures in closed chambers (the former at atmospheric pressure, the latter at about 5 atm), obtained ignition insofar as the mixture contained an excess of pentane, namely, between  $220^{\circ}$  and  $255^{\circ}$ . With an excess of air, they obtained only a sharp bend in the temperature-pressure curve, a sign that reaction had set in.

With excess of fuel, incipient luminescence was observed at about  $220^{\circ}$ , the intensity of which increases considerably at  $240^{\circ}$ , until at  $\sim 260^{\circ}$ , a rather bright "cold" flame appears which disappears at the end of the reaction chamber at which the burned gases leave and which wanders slowly toward the gas stream, thus traversing the chamber in about 1 sec (*i.e.*, with a velocity of 10 cm/sec). These flames follow one another at definite time intervals, but with rising temperature they

TABLE 89.—LUMINESCENCE AND COLD FLAMES IN PENTANE-AIR MIXTURES (FROM PRETTRE)

| % pentane<br>in air | Flow<br>velocity<br>1/per hr | $\Theta_1$ | $\Theta_2$ | $t_1$ | $t_2$ | $T, ^{\circ}C$ |
|---------------------|------------------------------|------------|------------|-------|-------|----------------|
| 2.6                 | 5.40                         | 225        | 237        | 263   | 285   | 672            |
| 4.05                | 6.50                         | 221        | 240        | 262   | 292   | 681            |
| 6.15                | 5.80                         | 225        | 235        | 261   | 286   | 710            |
| 11.8                | 6.20                         | 230        | 246        | 260   | 277   | No ignition    |

$\Theta_1$  = temperature at the beginning of luminescence.

$\Theta_2$  = temperature at which a great increase in intensity appears.

$t_1$  = beginning of the cold flames.

$t_2$  = end of the cold flames.

$T$  = ignition temperature.

<sup>1</sup> Cf. pp. 417–426.

<sup>2</sup> LEWIS, J. ST., *J. Chem. Soc.*, 1927, p. 1555; 1929, p. 759; 1930, p. 58.

<sup>3</sup> DUMANOIS, P., and MONDAIN-MONVAL, P., *Ann. Office nat. des combust. liquides*, **3**, 892 (1929); *Compt. rend.*, **187**, 892 (1928).

become slower and more diffuse until they disappear completely at about 290°. On the other hand, a luminescence remains with zones of maximum brightness, which wander slowly against the gas stream as in the experiments with lean mixtures. At 350°, only a luminescent oxidation, uniform over the entire tube, takes place. At 670° to 710°, ignition, as well as pulsating combustion, sets in at the gas entrance. This is clearly caused by the fact that flow velocity and normal combustion velocity are not attuned in such a manner that a static flame could maintain itself. Table 89 gives a survey of the phenomena in pentane.

That the cold flames always appear at the exit of the reaction chamber points to the fact that the gas mixture must first be prepared by a pre-reaction, *i.e.*, that a definite induction period is necessary up to the appearance of the cold flame (*cf.* pages 450ff.).<sup>1</sup>

Cold flames can also be recognized in a static apparatus, although with greater difficulty, induction periods of about 20 to 92 sec resulting.

In the higher hydrocarbons, the phenomena are analogous, but they appear at lower temperatures the longer the C-atom chain of normal paraffins is (*cf.* Table 90).

TABLE 90.—TEMPERATURES AT THE APPEARANCE OF LUMINESCENCE (FROM PRETTRE<sup>1</sup>)

| Propane,<br>°C | <i>n</i> -Pentane,<br>°C | <i>n</i> -Hexane,<br>°C | <i>n</i> -Heptane,<br>°C | <i>n</i> -Octane,<br>°C | Pentene,<br>°C | Cyclohexane,<br>°C | Cyclohexene,<br>°C | Benzol,<br>°C | Toluol,<br>°C |
|----------------|--------------------------|-------------------------|--------------------------|-------------------------|----------------|--------------------|--------------------|---------------|---------------|
| 225-270        | 225-242                  | 220-230                 | 210-230                  | 200-215                 | 260-270        | 235-260            | 255-260            | 670           | 600           |

<sup>1</sup> From the compilation in *Science*, **4**, 2953.

The table shows that, in the series of the *n*-paraffins, the temperature of the beginning of luminescence steadily drops with an increasing number of C-atoms but that this temperature rises in the transition to the corresponding olefin (pentane-pentene), just as it does in the transition from paraffin to naphthane (hexane-cyclohexane), that also in the cyclical compounds of unsaturated character the ability for reaction is again decreased (cyclohexane-cyclohexene), and that finally the aromatics are attacked a great deal more vigorously than all the other compounds.

We shall meet again and again the phenomenon that the unsaturated react with greater difficulty than the corresponding saturated (in contrast to the very first members of the series), and it obviously must be due to the fact that the double bond has a chain-breaking effect in the oxidation reaction, *cf.* page 388.

<sup>1</sup> In exceptional cases, *e.g.*, in ethyl ether, and lately also in paraffins, it is possible to obtain "cold flames" beginning at one point in a cold mixture, too, by means of suitable ignition; *cf.* p. 480.



Table 91 gives a survey of the behavior of the paraffins; the designations in it are the same as those above. The succession in which luminescence and the cold flames appear here with decreasing temperature is exactly the same as that of the decreasing knock resistance in the engine.

TABLE 91.—LUMINESCENCE, COLD FLAMES AND IGNITION OF PARAFFINS IN MIXTURE WITH AIR (FROM PRETTRE)

| Material                                    | % in air | $\Theta_1$ | $\Theta_2$ | $t_1$ | $t_2$ | Temperature, °C |
|---|----------|------------|------------|-------|-------|-----------------|
| CH <sub>4</sub>                             | 5.3      | 740        | —          | —     | —     | 770             |
|   | 18.5     | 690        | —          | —     | —     | 730             |
| C <sub>2</sub> H <sub>6</sub>               | 4.2      | 380        | 410        | —     | —     | 660             |
|   | 8.9      | 350        | 370        | —     | —     | 675             |
| C <sub>3</sub> H <sub>8</sub>               | 3.5      | 270        | 310        | —     | —     | 665             |
|   | 6.3      | 265        | 305        | —     | —     | 672             |
|   | 14.3     | 255        | 290        | 304   | 310   | No ignition     |
| C <sub>4</sub> H <sub>10</sub>              | 2.1      | 242        | 260        | —     | —     | 670             |
|   | 4.05     | 221        | 240        | 262   | 292   | 681             |
|   | 16.55    | 225        | 244        | 259   | 270   | No ignition     |
| C <sub>5</sub> H <sub>12</sub>              | 2.05     | 230        | 255        | —     | —     | 684             |
|   | 5.20     | 220        | 244        | 255   | 270   | 672             |
|   | 1.55     | 230        | 245        | —     | —     | 686             |
| C <sub>7</sub> H <sub>16</sub>              | 5.25     | 210        | 232        | 259   | 269   | 695             |
|   | 0.95     | 215        | 230        | —     | —     | 670             |
| C <sub>8</sub> H <sub>18</sub> <sup>1</sup> | 2.10     | 200        | 220        | 252   | 270   | 684             |

<sup>1</sup> At 252°, violent combustion.

The material of further observations, with which we shall become acquainted later, hardly leaves a doubt that the reactions observed here and those leading to knocking in the engine are identical.<sup>1</sup> This is specifically proved by the fact that it is possible to prove the existence of cold flames in engines, too.<sup>2</sup>

*Ethylene* shows an oxidation with luminescence only from 420° on and is therefore here, like the higher olefins, more stable in oxidation than paraffin; but in the engine it is less knock-resistant than ethane. Undoubtedly, wall influences, which are not present in the engine, play a role in the slow oxidation and in the cold flames, and an immediate correlation is therefore not always possible.

*Methanol* shows luminescence over a greater temperature interval in contrast to methane, beginning at about 395° to 410°. Ignition sets in, under Prettre's experimental conditions (in a flowing system), at 540° to 560°C.

<sup>1</sup> Naturally, this does not mean that they are identical in all details; the wall might, for example, have a greater importance than in the engine.

<sup>2</sup> PELETIER, L.A., S.G. VAN HOOGBRATEN, J. SMITTENBERG, and P.L. KOOYMAN, *Chaleur et ind.*, January, 1939.

*Ethanol* acts analogously; luminescence begins at 330° to 370° ignition at about 550° to 570°. At all temperatures, ethanol shows more intensive luminescence than ethane.

*Propanol* corresponds to ethanol; luminescence sets in at about 25° to 30° lower.

*Amyl alcohol* and *iso-amyl alcohol* act about the same; luminescence sets in at 300°, ignition at 510°. In mixtures very rich in alcohol, luminescence begins at 295° and increases rapidly. At 303° to 307° a very brilliant flame runs through the mixture, followed each time by a second less bright flame. The oxidation of the alcohols is similar to that of amylene, but under 300° it is much weaker than that of pentane and isopentane.

*n-Heptyl alcohol* shows luminescence from 260°; bright flames pass through fuel-rich mixtures between 275° to 277° and 280° to 290°. Above this, heptyl alcohol experiences only a slow oxidation, accompanied by a luminescence that is about as intense as that of heptane. The condensate of liquid reaction products of the higher alcohols contains, in addition to aldehydes, alcohols of low molecular weight.

Substituting OH for an H-atom in a hydrocarbon has the following effect, according to Prettre:

1. Increase of the oxidizability above 300°, especially in the first members of the series;
2. Decrease of the inclination to oxidation under 300°.

Of the aldehydes, *acetaldehyde* and *butyraldehyde* were investigated. According to Prettre, in all hydrocarbons that show the phenomenon of the cold flames, acetaldehyde represents the chief reaction product between 200° and 300°.

Acetaldehyde-air mixtures, with 5 to 45 per cent aldehyde, show luminescence from 200° to 210°. At 240°, this becomes very intensive, and "flaming" appears for all mixtures between 256° to 263° and 285° to 290°. The lively combustion of the mixtures with small surplus of aldehyde assumes an explosive form that is never observed in hydrocarbon-air mixtures. Above 285° to 290°, no flames appear any longer; normal ignition takes place at about 350° (*cf.* above, page 388).

Butyraldehyde acts entirely analogously; the phenomena also appear at about the same temperatures, except that regular ignition takes place at 400°.

Acetaldehyde in small concentration accelerates the oxidation of paraffin hydrocarbons in the range of luminescence.

The luminescence of ethyl ether has been known the longest (Perkin, cited page 437). It sets in at 170° to 180°; at 210°, it is visible even in an undarkened room; and, at 220° to 230°, depending on the concentration, cold flames set in, which in their intensity and velocity resemble

those in *n*-octane. With a further rise in temperature, these pass over continuously into the usual combustion toward 240° to 250°. The two ignition ranges present in hydrocarbons thus pass over into one another continuously. Acetaldehyde is produced in great quantities as well in slow oxidation as in lively combustion of ether-rich mixtures.

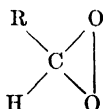
If the ethyl ether contains peroxide, a very violent explosion connected with the destruction of the apparatus sets in at the temperature at which luminescence would otherwise have begun, ~ 170°C. Before the explosion, no kind of luminescence is to be seen.<sup>1</sup>

Di-*n*-butyl ether is much more stable in oxidation than ethyl ether, which is very remarkable when we consider the action of the paraffins with increasing chain length, but which is supported by data on the knocking action of ethers. (Di-isopropyl ether, which can be technically obtained in great quantities as an initial product from cracked gases, is highly knock-resistant and is used in the manufacture of knock-resistant aviation gas.)<sup>2</sup> Nevertheless butyl ether acts like ethyl ether at low temperatures; however, normal ignition, depending on the experimental conditions, sets in only at 290° to 350°. In slow oxidation, aldehydes are likewise obtained in great quantities, among them chiefly butyraldehyde.

Acids seem to act like the alcohols, being perhaps somewhat more stable in oxidation than the latter.

The addition of peroxides (monoethyl hydroperoxide was investigated) has an accelerating effect on the oxidation of hydrocarbons (Prettre investigated *n*-butane); 0.6 per cent of this peroxide corresponded in its effectiveness to about 3 to 4 per cent of acetaldehyde. Peroxides of the same type (dimethyl peroxide, oxyethylmethyl hydroperoxide) have been proved to be present in the luminescent hexane oxidation in the neighborhood of 300°C by Mondain-Monval and Quanquin.<sup>3</sup>

Prettre<sup>4</sup> also investigated the influence of antiknock bodies, especially

According to Rieche, alkylidene peroxides of the form  are probably

responsible for the violent explosion [*Z. angew. Chem.*, **44**, 896 (1931)].

<sup>1</sup> Cf. Chap. XII, p. 559.

Cf. EGLOFF, *J. Inst. Petroleum Tech.*, **23**, 645 (1937). EGLOFF, W.H. HUBNER, and P.M. VAN ARSDELL, *Chem. Rev.*, **22**, 175 (1938).

<sup>3</sup> MONDAIN-MONVAL, P., and B. QUANQUIN, *Compt. rend.*, **189**, 917, 1194 (1929); **191**, 299 (1930); *Bull. soc. chim. ind. Mulhouse*, **96**, 265 (1930); *Ann. Office nat. des combust. liquides*, **5**, 307 (1930); *Ann. chim.*, (10), **15**, 309 (1931). Cf. also WHITE, A.G., and T.W. PRICE, *J. Chem. Soc.*, **115**, 1462 (1919).

Cf. in this connection the careful investigations by Egerton, Chap. XIII, pp. 540ff.

<sup>4</sup> PRETTRE, M., *Ann. Office nat. des combust. liquides*, **6**, 533 (1931).

of lead tetraethyl<sup>1</sup> on luminescence and the ignition of hydrocarbons. The investigations on the  $\text{Pb(eth)}_4$  effect on hydrocarbon oxidation made before Prettre seemed contradictory. According to the experiments of Dumanois, Aubert, and Pignot<sup>2</sup> as well as Lovell, Coleman and Boyd<sup>3</sup> on the velocity of lively combustion as well as of Bone,<sup>4</sup> Lewis<sup>5</sup> and Dumanois<sup>6</sup> and Mondain-Monval on slow combustion, there seemed to be an inhibition by antiknock compounds. On the other hand,  $\text{Pb(eth)}_4$  has no effect on the origin and velocity of the detonation wave, according to Egerton and Gates<sup>7</sup> as well as Dumanois and Laffitte.<sup>8</sup> However,  $\text{Pb(eth)}_4$  retards the combustion of 3 per cent pentane in air, according to Egerton and Gates.

The varied influence of antiknocks on ignition temperatures can, according to Prettre, be easily understood. All ignition temperatures that are so determined that their cold-flame range plays a role are greatly influenced by antiknocks, whereas those which are based on ordinary ignition at high temperatures are much less sensitive. In this manner, the apparent contradictions can be resolved.

Lead tetraethyl [in the form of ethyl fluid: 55 per cent  $\text{Pb(eth)}_4$ , 36 per cent ethyl bromide and 9 per cent monochlorine naphthalene] represses luminescence phenomena and cold flames in paraffins to a considerable extent. Luminescence appears only at higher temperatures than it does in pure fuels, and the cold flames do not appear at all (Table 92).

Benzol additions too (when added to pentane) act like lead tetraethyl but only in much higher concentrations, just as benzol is much less effective as an "antiknock" than is lead (*cf.* Chap. XII, page 567).

In connection with Prettre's investigations, *cf.* the observations of Townend and collaborators at higher pressures (pages 476ff.).

<sup>1</sup> Lead tetraethyl as the most effective "antiknock" was discovered by Midgley in 1922 [MIDGLEY, T., *SAE J.*, **1**, 7, 218, 374, 451 (1922); **4**, 589, 849 (1922)]. *Cf.* in addition WILSON, R.E., *Ind. Eng. Chem.*, **29**, 239 (1937). MIDGLEY, T., *Ind. Eng. Chem.*, **29**, 241 (1937).

<sup>2</sup> PIGNOT, A., *Compt. rend.*, **182**, 376 (1926). AUBERT, M., A. PIGNOT, and J. KILLEY, *Compt. rend.*, **185**, 1111 (1927). AUBERT, M., P. DUMANOIS, and A. PIGNOT, *Compt. rend.*, **186**, 1298 (1928).

<sup>3</sup> LOVELL, W.G., J.D. COLEMAN, and T.A. BOYD, *Ind. Eng. Chem.*, **19**, 373 (1927).

<sup>4</sup> BONE, W.A., and DRUGMAN, *J. Chem. Soc.*, **89**, 660, 939 (1906). BONE, DRUGMAN, and ANDREWS, *J. Chem. Soc.*, **89**, 1614 (1906).

<sup>5</sup> LEWIS, J.ST., *J. Chem. Soc.*, **132**, 759 (1929); **135**, 58 (1930); **136**, 1555 (1927).

<sup>6</sup> DUMANOIS, P., and P. MONDAIN-MONVAL, *Compt. rend.*, **187**, 892 (1928); *Ann. Office nat. des combust. liquides*, **3**, 892 (1929).

<sup>7</sup> EGERTON, A.C., and S.F. GATES, *J. Inst. Petroleum Tech.*, **13**, 244, 256, 273, 281 (1927); *Proc. Roy. Soc. London, A*, **114**, 137, 152 (1927); **116**, 516 (1927).

<sup>8</sup> DUMANOIS, P., and P. LAFFITTE, *Compt. rend.*, **186**, 146 (1928).

TABLE 92.—INFLUENCE OF LEAD TETRAETHYL ON THE OXIDATION BEHAVIOR OF HYDROCARBONS (FROM PRETTRE)

| Hydrocarbon | Ethyl fluid<br>% in hydro-<br>carbon | % hydro-<br>carbon<br>in air | $\Theta_1$ | $\Theta_2$ | $t_1$    | $t_2$ | Tempera-<br>ture, °C |
|-------------|--------------------------------------|------------------------------|------------|------------|----------|-------|----------------------|
| $C_5H_{12}$ | 0.4                                  | 2.35                         | 310        | 345        | No flame |       | 670                  |
|             | 0.4                                  | 3.85                         | 340        | 364        | No flame |       | 710                  |
|             | 0.4                                  | 6.75                         | 310        | 350        | No flame |       | No ignition          |
|             | 0.4                                  | 11.55                        | 287        | 330        | No flame |       | No ignition          |
| $C_6H_{14}$ | 0.4                                  | 4.05                         | 280        | 290        | No flame |       | 748                  |
|             | 0.4                                  | 8.65                         | 291        | 310        | No flame |       | No ignition          |
|             | 0.6                                  | 4.15                         | 335        | 370        | No flame |       | 751                  |
| $C_7H_{16}$ | 0.4                                  | 3.70                         | 265        | 270        | No flame |       | 741                  |
|             | 0.6                                  | 4.10                         | 300        | 320        | No flame |       | No ignition          |
|             | 0.8                                  | 3.95                         | 360        | 405        | No flame |       | No ignition          |

*b. More Accurate Investigations of Cold Flames in Pentane.*—In addition to the works by Prettre on the problem of the mechanism of cold flames, the studies of Neumann and Aivazov<sup>1</sup> on pentane, which we shall now discuss, are especially informative.

Pentane-oxygen mixtures in oxidation show the phenomenon of the negative temperature coefficient (*cf.* page 428) to a decided extent (*cf.* Fig. 209, which at the same time shows how much the reaction velocity increases with the pressure).

In the more exact investigations, a cylindrical quartz chamber 25 cm in length was used which could be observed through a window in an electric oven. The gases were premixed and then introduced into the evacuated reaction chamber. The pressure in the reaction chamber was measured by means of a glass-membrane manometer whose sensitivity was 0.03 mm Hg. A typical pressure variation with the appearance of cold flames is reproduced in Fig. 204. Section *AB* represents the last part of the warming of the mixture to the reaction temperature. After that, the pressure remains constant for a time and then rises, at first slowly, then very rapidly, *CD*. The interval *CD* represents the appearance of cold flames. After that, the pressure at first drops rapidly, *DE*, and then rises slowly and steadily. The experiment refers to a mixture of  $C_5H_{12} + 4O_2$  at 300 mm Hg and 318°C. The induction period  $\tau$  is computed as the time from the entrance of the mixture to the sudden rise in pressure *C*.

<sup>1</sup> NEUMANN, M.B., and B.V. AIVAZOV, *Nature*, **135**, 655 (1935); *Acta Physicochim. URSS*, **4**, 575 (1936); *Z. physik. Chem.*, Sec. B, **33**, 349 (1936). ANDREEV, E.A., *Acta Physicochim. URSS*, **6**, 57 (1937). AIVAZOV, B.V., and M.B. NEUMANN, *Acta Physicochim. URSS*, **6**, 279 (1937). *Cf.* also EGERTON, A., and PIDGEON, *J. Chem. Soc.*, 1932, pp. 661, 676.

The appearance of the cold flames was observed in a special oven with a window over the entire length. The cold flame always appears at the hottest place of the reaction chamber, no matter whether this happens to be at either end or in the middle. It moves with a velocity of about 10 cm/sec.<sup>1</sup> The flame has the form of a cone with the apex in the direction of propagation and a width of about 3 cm; it therefore occupies about 10 per cent of the reaction chamber.

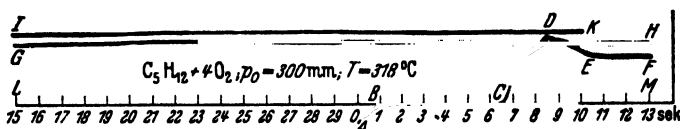


FIG. 204.—Pressure recording at the appearance of cold flames in pentane-oxygen mixtures. Compare the text. (From Neumann and Aivazov, p. 437.)

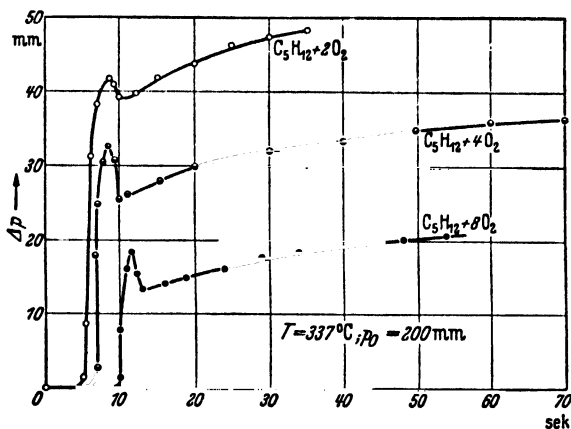


FIG. 205.—Appearance of cold flames in various pentane-oxygen mixtures. The first steep pressure rise corresponds to the appearance of the cold flame. (From Neumann and Aivazov, p. 437.)

More exact experiments showed that the appearance of the cold flames corresponds to point C, and the disappearance to point E. The drop in pressure from D to E therefore probably corresponds to the cooling of the gases behind the flame front. With this assumption and the observation that the cold flame comprises about 10 per cent of the entire gas volume, it is possible to compute from the observed decrease in pressure DE, in a particular case of 12 mm, that the temperature in the cold flame had risen about  $200^\circ$  to  $250^\circ$  above that of the chamber walls. Aivazov and Neumann mention unpublished experiments by Skalov, according to which direct measurements of cold flames in ether are said to have yielded the same rise in temperature.

<sup>1</sup> Approximately the same velocity is observed also in other cases (cf. pp. 438 and 482).

In this case, as in others too, reproducible results are obtained only if a series of experiments is carried out in the same reaction chamber one after the other. Figures 205 and 206 show several typical experiments in the cold-flame range with varied initial pressure as well as varied composition of the mixture. Raising the pressure shortens the induction period, increases the pressure rise in the cold flame, and accelerates the reaction after the cold flame. Overenriching the mixture has an analogous effect. Gas analyses showed that practically no conversion can be demonstrated during the induction period. CO is produced up to about 10 per cent of volume during the cold flame. In the period after the passage of the cold flame, the CO amount rises uniformly to about 30 to 35 per cent, whereas only a little  $\text{CO}_2$  ( $\sim 1$  per cent) is formed. Toward

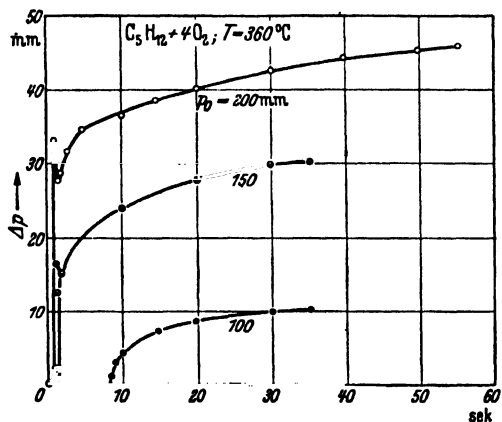


FIG. 206.—Appearance of cold flames in  $\text{C}_5\text{H}_{12} + 4\text{O}_2$  at various pressures. (From Neumann and Aivazov, p. 437.)

the end of the induction period, aldehydes can be demonstrated by means of Schiff's reagent; their concentration increases considerably during cold flames. Peroxides (proved by means of KI and  $\text{H}_2\text{SO}_4$ ) were present only in traces at the end of the induction period but were very clearly present after the passage of the cold flame.

The reaction products of 20 experiments were collected in a trap with 5  $\text{cm}^3$  of water and analyzed. For experiments with  $\text{C}_5\text{H}_{12} + 2\text{O}_2$  at 300 mm initial pressure and  $318^\circ\text{C}$ , the results reproduced in Fig. 207 were obtained. The aldehydes found seem to be chiefly lower aldehydes. The analyses show quite clearly that the drop in pressure after the passage of the cold flames should be attributed not to a chemical reaction taking place with a decrease in mol-number but rather actually to a decrease in temperature.

For the appearance of cold flames, there is, under predetermined conditions, a certain minimum pressure. Thus it is shown also in this

case that the cold flames bear all the external marks of true explosion but do not need to develop to complete combustion. The critical pressure limits depend to a large extent on the material of the wall.

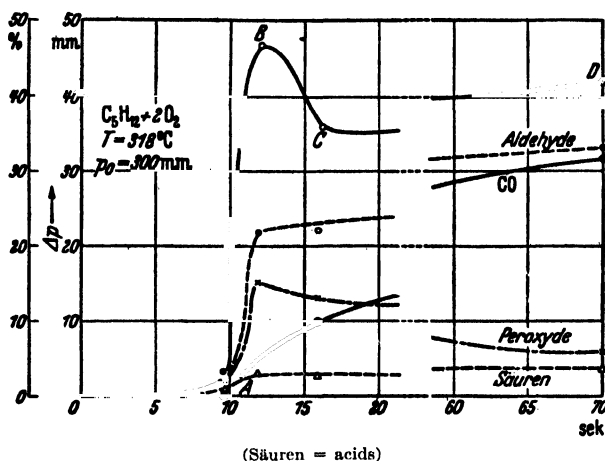


FIG. 207.—Concentration of the reaction products during the oxidation of pentane (ordinate values = per cent) and change in pressure (mm Hg). (From Aivazov and Neumann, p. 437.)

The pressure necessary for the appearance of cold flames was considerably reduced if the glass container was replaced by one of quartz<sup>1</sup> of the same size (Table 93).

TABLE 93.—RANGE OF THE COLD FLAMES FOR  $C_5H_{12} + 4O_2$  IN CHAMBERS WITH A DIAMETER OF 20 MM, MINIMUM PRESSURES

| $t^\circ C$ .....       | 304 | 320 | 330 | 340 | 370 | 400 | 430 | 450 |
|-------------------------|-----|-----|-----|-----|-----|-----|-----|-----|
| $p$ , mm Hg quartz..... | 300 | 175 | 140 | 115 | 85  | 100 | 130 | 140 |
| $p$ , mm Hg glass.....  | —   | 300 | 212 | 170 | 110 | 100 | 130 | 175 |

If  $Pb(eth)_4$  was introduced into the reaction chamber at 0.2 mm of pressure and the chamber thereupon carefully evacuated, the walls were changed to such an extent that the limits were displaced to  $40^\circ$  higher temperatures. In the neighborhood of the limits, it is often possible to observe several stages in the rise in pressure instead of a single rise. This might be due to the fact that the cold flame appears at one place but is then extinguished because the rest of the mixture has not yet reacted far enough until, after a certain interval (1 to 5 sec), the cold flame has formed anew in the remaining mixture. A similar phenomenon was observed by Munro<sup>2</sup> in the reaction of propane with oxygen.<sup>3</sup>

<sup>1</sup> Wall reactions of the peroxides?

<sup>2</sup> MUNRO, *J. Am. Chem. Soc.*, **57**, 1053 (1935).

<sup>3</sup> Cf. also HSIEH, M.S., and D.T.A. TOWNEND, *J. Chem. Soc.*, 1939, pp. 332, 337, 341.



The dependence of the critical pressure limits on the diameter of the container is shown in Fig. 208. The position of the limits is only little dependent on the composition of the mixture. The mixtures  $C_5H_{12} +$

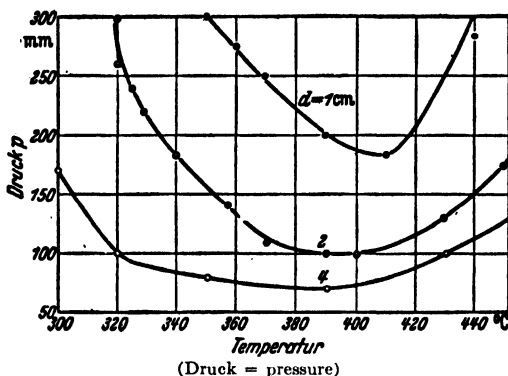


FIG. 208.—Critical pressure limits for pentane-oxygen mixtures for various temperatures and chamber diameters from Neumann and Aivazov.

$4O_2$ ,  $C_5H_{12} + 2O_2$ , and  $C_5H_{12} + O_2$  yielded practically the same limits in a quartz container.

Semenoff<sup>1</sup> has derived from Egerton and Pidgeon's<sup>2</sup> experiments for the variation in time of pentane oxidation (with  $C_5H_{12} + 4O_2$  between 260° and 280°C) below the limit of cold flames ( $w$  reaction velocity)

$$w = Ae^{\Phi t}$$

with

$$\Phi = \text{const } p^3 e^{-35,500/T}$$

Whether real importance attaches to this high value of the heat of activation of 71 kcal seems doubtful (*cf.* pages 449–450).

Aivazov and Neumann conducted experiments above the range of cold flames with  $C_5H_{12} + 8O_2$  and  $C_5H_{12} + 4O_2$  at about 500°C. The course of the velocity was of the auto-catalytic type, as with Egerton and Pidgeon and many other examples. For  $\Phi$  in the formula

$$\Delta p = Ae^{\Phi t}$$

we obtain

$$\Phi = k \cdot p^{3.4} e^{-16,800/T}$$

The value of 32.6 kcal for the activation energy perhaps appears more plausible. With a rise in pressure and temperature, the degenerate explosion passes over into a real explosion. The latter took place, for example, at 200 mm pressure and 568°C after an induction period of 7 sec.

Aivazov and Neumann regard the difference between the activation energy derived by them for higher temperatures and that derived from Semenoff and Egerton's experiments as an argument for the fact that a

<sup>1</sup> SEMENOFF, "Chemical Kinetics and Chain Reactions," Oxford, 1935.

<sup>2</sup> EGERTON and PIDGEON, *J. Chem. Soc.*, 1932, pp. 661, 676.

different reaction mechanism is present at higher and at lower temperatures. The apparent activation energies thus determined appear to

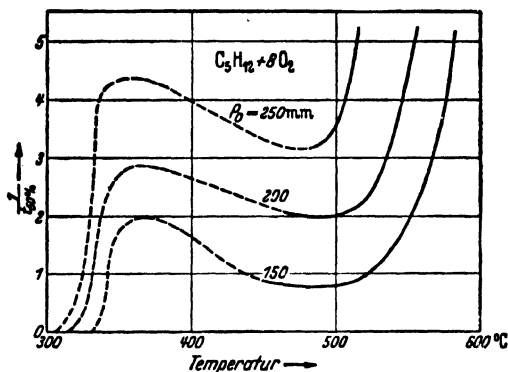


FIG. 209.—Reaction of pentane with oxygen in dependence on the temperature, reciprocal half-life period as measure. (From Neumann and Aivazov, p. 437.)

us to be too uncertain to warrant any extended conclusions. Nevertheless, so many facts suggest that the reaction mechanism is a different one at high temperatures than at low that the conclusion of Aivazov and Neumann might nevertheless be valid.<sup>1</sup>

The temperature dependence of the reaction velocity expressed by the reciprocal half-life span is presented in Fig. 209 for  $C_5H_{12} + 8O_2$  at various pressures. Between 360° and 480°, there is a negative temperature coefficient; caution is necessary in judging the reaction velocity in this range, since we are perhaps always dealing with nonstatic reactions (*cf.* also *n*-heptane, Beatty and Edgar, cited page 454).

Simple formal relations are valid for the induction periods up to the appearance of the cold flames, at least under the conditions of the experiments of Aivazov and Neumann.<sup>2</sup> For the dependence on temperature, the following is valid:

$$\tau = \text{const } e^{+\gamma/T}$$

Here  $\gamma$  is still dependent on the pressure, however. For  $C_5H_{12} + 4O_2$ , for example, with  $p = 200$  mm Hg,  $\gamma = 64,000$ , whereas with 150 it is only 56,000. This and the absolute height—from this an activation energy of over 100 kcal would result—show that

<sup>1</sup> However, it must be kept in mind that at higher temperatures the reaction of the intermediary products, especially CO, can be determining.

<sup>2</sup> AIVAZOV, B., and M. NEUMANN, *Z. physik. Chem.*, Sec. B, **33**, 349 (1936).

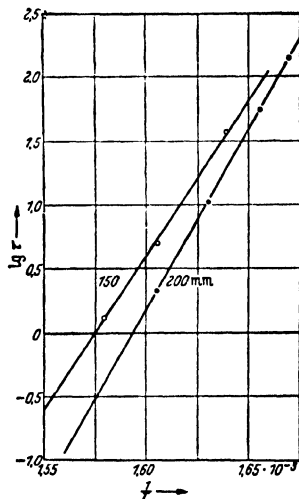


FIG. 210.—Induction periods for cold flames in pentane, s. For  $C_5H_{12} + 4O_2$ . (From Neumann and Aivazov, p. 437.)

it can only be a matter of the apparent activation energy of a composite process. Numerical values for the induction periods are obtained from Fig. 210.  $\tau$  is, as also in other cases, approximately inversely proportional to a power of the pressure, in a manner that makes

$$\tau(p - p_0)^n = \text{const}$$

with  $n$  about = 2.  $p_0$  is the limit pressure for the appearance of cold flames. For 350°C and  $\text{C}_5\text{H}_{12} + 4\text{O}_2$ , there is valid, if the pressure is measured in mm Hg,

$$\tau(p - 95)^2 = 22,500$$

Likewise in agreement with other findings, it is found that an increase in the pentane concentration greatly shortens the induction period (Table 94).

TABLE 94.—INDUCTION PERIOD  $\tau$  FOR  $\text{C}_5\text{H}_{12} + x\text{O}_2$  AT 200 MM HG AND 337°C (FROM NEUMANN AND AIVAZOV)

| $x$ .....         | 1     | 2    | 4   | 8    | 9     | 12   | 16  |
|-------------------|-------|------|-----|------|-------|------|-----|
| $a^1$ .....       | 0.125 | 0.25 | 0.5 | 1    | 1.125 | 1.5  | 2.0 |
| $\tau$ , sec..... | 4.1   | 5.4  | 6.6 | 10.2 | 11.8  | 18.4 | —   |

<sup>1</sup>  $a$  = excess oxygen factor =  $x/8$  (a pentane requires  $8\text{O}_2$  for complete combustion).

The minimum for  $\tau$  lies about at  $a = 0.1$ , a range in which a normal flame is no longer able to propagate.

In dependence on the diameter of the container, the following induction periods were determined (Table 95).

TABLE 95.—INDUCTION PERIOD FOR COLD FLAMES IN  $\text{C}_5\text{H}_{12} + 4\text{O}_2$  WITH VARYING CHAMBER DIAMETER AT 300 MM HG AND 390°C

| $d$ , cm..... | 1   | 2   | 4                |
|---------------|-----|-----|------------------|
| $\tau$ .....  | 2.2 | 1.2 | 1.0 <sup>1</sup> |

<sup>1</sup> In this experiment, the cold flame passed over into regular explosion.

Prettre<sup>1</sup> finds for the induction period up to ignition in pentane-oxygen mixtures

$$\tau p_{\text{KW}}/p_{\text{total}}^2 = \text{const}$$

where  $p_{\text{KW}}$  is the partial pressure of the hydrocarbon and  $p_{\text{total}}$  is the total pressure. The apparent activation heat determining for temperature dependence is found to be very high (80 to 100 kcal).

That reaction chains at the wall are broken off is also shown by the influence of nitrogen additions. Aivazov and Neumann have made experiments to this effect on butane, but the results are certainly valid qualitatively also for pentane. Figures 211 and 212 show the induction periods for  $\text{C}_4\text{H}_{12} + \text{O}_2$  with various nitrogen additions in dependence on the one hand on the partial pressure ( $\text{C}_4\text{H}_{10} + \text{O}_2$ ) and on the other

<sup>1</sup> PRETTRE, M., *Ann. Office nat. des combust. liquides*, **11**, 669 (1936); very inclusive experimental material is found here.

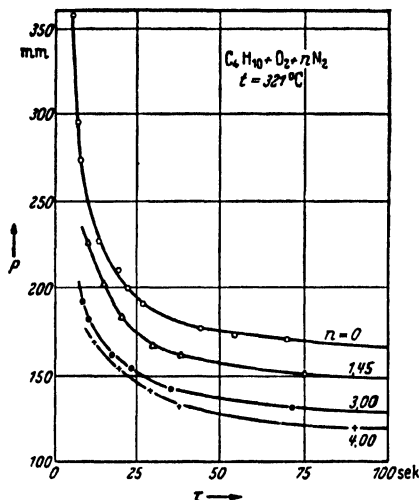


FIG. 211.—Induction periods of butane-oxygen mixtures for various pressures and nitrogen additions. (From Neumann and Alcazar, p. 437.)

hand on the induction period for a mixture  $C_4H_{10} + O_2$  at 380 mm Hg in dependence on the temperature  $N_2$  additions. Formally the following is valid:

$$\tau(a + b[N_2])^2 = \text{const}$$

By various additions, the induction period is reduced; acetaldehyde also belongs here, but it is relatively weak in its effect. One per cent acetaldehyde for a mixture of  $C_5H_{12} + 2O_2$  reduces the induction period by about 40 per cent; 5 per cent aldehyde (i.e., about 15 per cent for hydrocarbon) decreases it from 14 to about 4 sec.

Much more effective is  $NO_2$ , which, for example, in a mixture of  $C_5H_{12} + 2O_2$  at  $318^\circ C$  and 210 mm Hg in a glass container having a diameter of 3 cm, reduces the induction period from 75 to 22 sec, if it is added in a concentration of only 0.004 per cent.

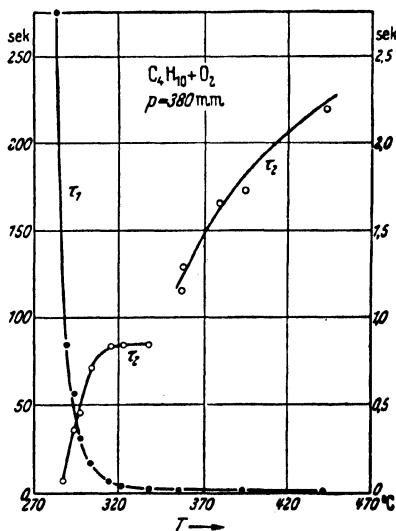


FIG. 212.—Induction periods for the appearance of cold flames.  $\tau_1$ , left scale, as well as for regular ignition.  $\tau_2$ , right scale. (From Andreev.<sup>1</sup>)

<sup>1</sup> ANDREEV, E.A., *Acta Physicochim. URSS*, 6, 57 (1937).

Aivazov and Neumann emphasize that there is no static but rather an auto-accelerated reaction even outside the range of the cold flames. On the basis of Semenov's theory (page 444), they give a derivation of the formal relations obtained, but its significance is difficult to estimate.

It is reasonable to suppose, on the basis of the curves (*e.g.*, in Fig. 209) as well as the individual observations of true explosions, that, with small additional rises in pressure or an increase in the hydrocarbon concentration in the range of the velocity maximum, the "cold flame" will pass over into true explosion. It will especially be expected that, at high pressures as they are employed in explosion engines, ignition temperatures will be obtained in the same neighborhood as for cold flames or even below. This is actually the case, as has been shown in the experiments of Tizard and Pye,<sup>1</sup> which yielded ignition temperatures down to about 280°C for *n*-heptane.

An answer to this problem as well as to the transition from cold flames to regular ignition is given in a further work by Neumann and Aivazov.<sup>2</sup> Andreev<sup>3</sup> has shown in the case of butane how a cold flame can pass over into normal explosion, and that as a result the explosion is a two-staged process. He used mixtures of  $C_4H_{10} + O_2$ , the explosion proceeding without destroying the apparatus. A quartz reaction chamber was used, likewise in connection with a recording glass-membrane manometer. Above a certain limit (*e.g.*, at 360 mm Hg and 321°C), a normal ignition takes place. In this case, after introducing the gas into the reaction chamber, there is a first certain induction period,  $\tau_1$ , until the appearance of the cold flame with a corresponding rise in pressure, then a further induction period,  $\tau_2$ , until a new sudden rise in pressure indicates regular ignition. The most striking fact in this connection is that this second induction period increases with rising temperature.<sup>4</sup> In Fig. 212 from Andreev, the induction periods  $\tau_1$  (up to the appearance of the cold flame) and  $\tau_2$  (from the appearance of the cold flame up to regular ignition) are plotted for  $p = 380$  mm.  $\tau_1$  decreases considerably with the increasing temperature, while  $\tau_2$  rises from about  $\frac{1}{10}$  sec at 285° to over 2 sec at 440°C. At low temperatures (below 320°),  $\tau_1$  is preponderantly determining for the entire induction period up to ignition; it rises from several seconds to 275 sec at  $\sim 275^\circ$ . Between 336° and 352°, the curve for  $\tau_2$  is interrupted. In this case, only cold flames and no regular ignitions appear.

Various conjectures regarding the lengthening of  $\tau_2$  with increasing temperature are possible. It is not improbable—and Andreev assumes

<sup>1</sup> TIZARD, H.T., and PYE, *Phil. Mag.*, **44**, 79 (1922).

<sup>2</sup> AIVAZOV, B.V., and M.B. NEUMANN, *Acta Physicochim. URSS*, **6**, 278 (1937).

<sup>3</sup> ANDREEV, E.A., *Acta Physicochim. URSS*, **6**, 57 (1937).

<sup>4</sup> Less reactionable reaction products appear (?).

this also—that with rising temperature the nature of the reaction products formed in the cold flames changes (that in place of aldehydes, especially formaldehyde, their essentially more stable disintegration products, especially  $H_2$  and  $CO$ , appear). It is further to be considered that the reactions preparing ignition begin during the induction period of the cold flames, for which purpose more time would naturally be available at low temperatures and long  $\tau_1$ .

Neumann and Aivazov (cited page 452) have investigated these conditions more exactly for pentane; cf. also Neumann and Tutakin.<sup>1</sup> We shall report in detail an experiment that ended with a violent explosion. Mixtures:  $C_5H_{12} + 4O_2$  at 340 mm Hg and  $318^\circ C$ .

|                   |   |   |     |     |     |     |     |     |           |
|-------------------|---|---|-----|-----|-----|-----|-----|-----|-----------|
| $t$ , sec =       | 0 | 8 | 8.2 | 8.4 | 8.6 | 8.8 | 9.0 | 9.2 | 9.21      |
| $\Delta p$ , mm = | 0 | 0 | 2   | 35  | 48  | 52  | 54  | 57  | Explosion |

The induction period  $\tau_1$  for the cold flame in this case was 8.2 sec; the induction period from there on up to regular explosion,  $\tau_2$ , was a further 1.01 sec. The cold flame had progressed in the 30 cm long quartz chamber with a velocity of 7 to 10 cm/sec. The normal flame took its inception beyond the front of the cold flame, at the same place where the latter had begun. The velocity of the hot flame is of the order of magnitude of 500 to 1000 m/sec.\*

In order that the cold flame can pass over into a hot one, a certain higher critical pressure at a given temperature is required. In Table 96, the critical pressure limits for cold and hot flames for a quartz container 20 mm in diameter are given.

TABLE 96.—CRITICAL PRESSURE LIMITS FOR COLD FLAMES ( $p_k$ ) AND FOR REGULAR EXPLOSION ( $p_e$ ) OF  $C_5H_{12} + 4O_2$

|                               |     |     |     |     |     |     |     |     |
|-------------------------------|-----|-----|-----|-----|-----|-----|-----|-----|
| Temperature, $^\circ C$ ..... | 304 | 305 | 310 | 320 | 340 | 360 | 400 | 440 |
| $p_k$ , mm Hg.....            | 300 | 250 | 220 | 175 | 115 | 85  | 100 | 130 |
| $p_e$ , mm Hg.....            | —   | —   | 360 | 335 | 325 | 337 | —   | —   |

Neumann and Tutakin have found that additions of nitrogen shorten the induction period of cold flames. For a mixture of  $C_4H_{10} + O_2 + nN_2$  (with  $p_{C_4H_{10}+O_2} = 213$  mm Hg) at  $321^\circ C$ , the following resulted:

|                |    |     |      |      |      |     |     |
|----------------|----|-----|------|------|------|-----|-----|
| $n$ =          | 0  | 0.3 | 0.5  | 1    | 1.5  | 2   | 4   |
| $\tau$ , sec = | 32 | 22  | 18.5 | 14.3 | 11.5 | 9.4 | 4.5 |

<sup>1</sup> NEUMANN, M., and P. TUTAKIN, *Compt. rend. acad. sci. URSS*, **4**, 122 (1936).

\* This might mean that it is not a matter of so high a flame velocity, but rather the explosion takes place almost simultaneously in the entire container. Cf. the observations for oxygen-hydrogen by P. Tauzin, *Ann. phys.*, (11), **6**, 575 (1926); cf. p. 306.

Ammonia additions also had an analogous effect. There can thus be no doubt that we are dealing with a chain reaction with breaking at the wall. The same is also true for the succeeding reaction of the two-stage process. Also the second induction period that passes between the cold flame and regular ignition is shortened by the addition of nitrogen. Even though at these low pressures the processes leading to ignition are to be understood as a pure chain explosion, it is naturally not excluded that, at the higher pressures that are employed in engine combustion, heat production also essentially aids the reaction. According to more recent experiments,<sup>1</sup> inert gas additions at 470 mm pressure lengthen the induction period for the transition of the cold flame to regular ignition, which proves that, at higher pressures, a thermal process is determining in this case, whereas the appearance of the cold flames is conditioned by chain-branching. Since ammonia additions yield the same inert gas influence as nitrogen in the case of cold flames, Neumann and Tutakin<sup>2</sup> conclude that aldehyde is not decisive for the appearance of cold flames.

For the transition of the cold flame into a true explosion, cf. particularly Prettre.<sup>3</sup>

*c. The Oxidation of Higher Hydrocarbons.*—Edgar<sup>4</sup> and his collaborators studied, by means of a flow apparatus, the oxidation of *n*-octane, heptaldehyde, and butyraldehyde with air in stoichiometric mixture; later, they also studied that of isomeric octane. An analysis of the reaction products showed in an experiment at 260° that, among the condensable substances per mol of permeated octane, there were 0.55 unoxidized octane, 0.33 aldehyde, 0.25 acid, 0.07 peroxide, and 0.36 water. With increasing temperature, the peroxides and acids disappeared. Of the gaseous products, of course, CO and CO<sub>2</sub> were predominantly present.

Because of the reaction heat, the temperature in the pyrex reaction tube about 25 mm in diameter and 900 mm in length showed a sharp rise behind the gas intake. The main conversion took place in the first section of the reaction space; in the consumption of oxygen, there was no essential difference whether the gas tests were taken at 20 per cent of the oven length behind the intake or at the farthest end of the oven. The flow velocity was chosen in all experiments so as to yield a reaction duration of about 50 sec at 200° and 25 sec at 650°. Up to about 200°,

<sup>1</sup> AIVAZOV, B., M. NEUMANN, and I. CHANOVA, *Acta Physicochim. URSS*, **9**, 767 (1938).

<sup>2</sup> NEUMANN, M.B., and P.M. TUTAKIN, *Acta Physicochim. URSS*, **9**, 861 (1938).

<sup>3</sup> PRETTRE, M., *Ann. Office nat. des combust. liquides*, **11**, 669 (1936).

<sup>4</sup> POPE, J.C., F.J. DYKSTRA, and G. EDGAR, *J. Am. Chem. Soc.*, **51**, 1875, 2203, 2213 (1929). BEATTY, H.A., and G. EDGAR, *J. Am. Chem. Soc.*, **56**, 102, 107, 112 (1934).

no oxygen consumption could be proved, but between 200° and 270° the latter rose until about 2 mols of O<sub>2</sub> per mol of octane were consumed.

At 270°, pulsations appeared in the gas flow that coincided with the appearance of the cold flames described in the previous section. These succeeded each other at first in stages of 10 to 15 sec, then more frequently but becoming weaker until at 300° to 325° no pulsations were to be observed any longer. In this range, the thermo-element can show up to 100° more at the gas intake than at the exit. The consumption of oxygen increases rapidly up to 350° and after that more slowly—from 350° to 650°, about 1 mol per mol of octane. Up to 650°, 6 mols per mol of octane are consumed in all. Above 650°, ignition sets in. Only few

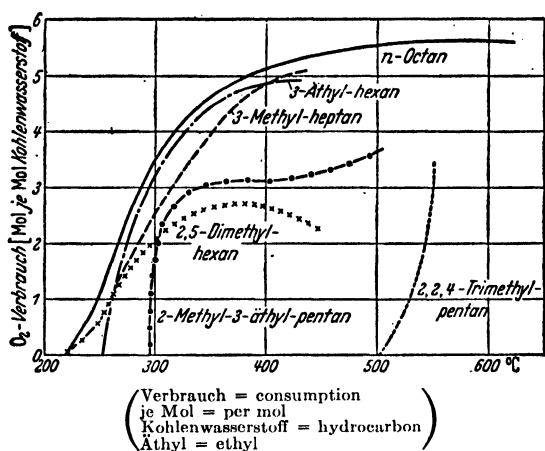


FIG. 213.—Oxidation of isomeric octane with air in stoichiometric mixture. (From Edgar and associates, p. 447.)

gaseous reaction products appear between 200° and 270°, principally CO<sub>2</sub>, probably as the result of a wall reaction. Above this point, a stronger increase in CO formation appears until at 650° about 3.5 mols of CO are produced per mol of octane.

In these special experiments (cf. Fig. 213), no negative temperature coefficient was observed but instead only a very small positive temperature coefficient. Since, by means of a minor variation in the experimental conditions (*e.g.*, lengthening the reaction duration), the temperature coefficient for the total conversion can change from a negative to a small positive value (cf. page 466), this fact is to be accorded no importance. An abnormally small positive temperature coefficient has the same cause as a negative temperature coefficient.

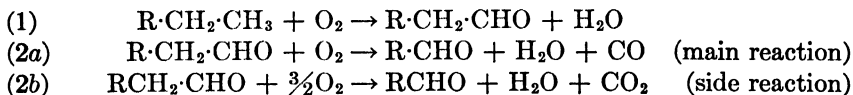
Heptaldehyde begins to combine with O<sub>2</sub> at 150°C; there is a sharp rise of O<sub>2</sub> consumption with the temperature, although it is a little less than with octane. At 300°, this rise is almost zero; then follows another



slight rise. From the very beginning, CO and CO<sub>2</sub> appear together; at 235°C, about 0.5 mols (per mol of aldehyde) of each are present. Then the pulsations and luminescence appear, the CO content increases to about 2 mols at 275° (pure aldehyde does not yet produce CO by its auto-disintegration at these temperatures); and the CO<sub>2</sub> content rises only slowly and steadily also above 235°.

*Butyraldehyde* acts analogously; however, a considerable rise in velocity and pulsations is noticeable at only 325°.

Edgar and his collaborators assume two gross reactions:



The empirical consumption fits these assumptions; in particular octane, on account of reaction (1), consumes 1 mol of O<sub>2</sub> more than the aldehyde (per mol of fuel).

The empirical O<sub>2</sub> consumption therefore suggests the assumption that aldehyde appears as the first stable intermediary product, which is then built up to the aldehyde, which is poorer by one C-atom. This includes the assumption that the carbon atom chain is oxidized from the end, which is in agreement with all the other experiences in the oxidation of gaseous hydrocarbons.<sup>1</sup> Alcohols probably do not come into consideration here as intermediary products of normal oxidation. According to Layng and Youker,<sup>2</sup> *n*-heptyl alcohol is relatively difficult to oxidate.<sup>3</sup>

The oxidation behavior of isomeric octanes is shown by Fig. 213.

<sup>1</sup> On the other hand, it is noteworthy that, in the oxidation of paraffins in the liquid stage to fatty-acid synthesis [cf. G. Wietzel, *Z. angew. Chem.*, **51**, 531 (1938)], the reaction products are extensively straight-chained, even though the paraffin used was branched. This can most easily be explained by assuming that the attack of the oxygen on the tertiary C-atom took place with splitting off of the side chains. That something similar does not take place in the gas phase must be concluded from the fact that branched paraffins are more stable in oxidation and more knock-resistant than straight-chained paraffins are. The difference in the action of liquid and gaseous substances need not perhaps be very surprising; sometimes ion reactions play a role in the liquid phase which in the gas phase could enter the picture at the most only at the wall.

<sup>2</sup> LAYNG, T.E., and M.A. YOKER, *Ind. Eng. Chem.*, **20**, 1048 (1928).

<sup>3</sup> Not many exact measurements have been published on the oxidation behavior of the alcohols. According to the data at present available, also in respect to knock behavior (cf. the next chapter), the following seems to hold for alcohols (and is, by the way, valid also for olefins): The lowest alcohols and olefins are less stable in oxidation than the corresponding paraffins, but the decrease in oxidation stability with an increasing number of C-atoms *n* is less marked for alcohols and olefins than for paraffins. For that reason, a crossing takes place, about in the range *n* = 4, and the higher alcohols and olefins are more stable in oxidation (at least in the gas phase) and more knock-resistant than the corresponding paraffins.

In *n*-octane, the O<sub>2</sub> consumption had been quite exactly equal to (1 + 1 mols of CO formed +  $\frac{3}{2}$  mols of CO<sub>2</sub> formed) per mol of octane. Isomeric octanes (except 2,2,4-trimethyl pentane) show a similar behavior, and an analogous course of reaction by way of aldehydes might therefore also be assumed. The primary attack would have to take place on the methyl group with the longest lateral chain, because the O<sub>2</sub> consumption during the first sharp rise in velocity approximately corresponds to the disintegration of this chain.

Cold flames are observed only in 3-methyl heptane and 3-ethyl hexane. Since conversion is much smaller in 2-methyl-3-ethyl pentane and 2,5-dimethyl hexane, it might be a matter merely of a quantitative difference, for the temperature variations of the oxidation are otherwise still analogous (Fig. 213). Only 2,2,4-trimethyl pentane varies completely, since oxidation begins only at  $\sim 500^\circ$ ; but it begins very rapidly. In those cases in which no cold flame is observed, only one atom of C appeared in the gaseous oxidation products.

Taking *n*-heptane as an example, Beatty and Edgar (cited page 454) have made a detailed study of the phenomena to be observed in oxidation. They used a pyrex chamber 2.41 cm in diameter and 65 cm in length. The gases, in stoichiometric composition, flowed through the chamber with a time of stay of  $\sim 40$  sec at  $200^\circ$  and of 23 sec at  $550^\circ\text{C}$ . The temperature could be measured at various intervals from the intake

of the gas, and the exhaust gases could also be drawn off at various intervals. It was shown that, from  $\sim 265^\circ$  upward, a considerable rise in temperature appeared behind the gas intake, by up to  $\sim 75^\circ$  above the average oven temperature (Fig. 214).

The analysis values of gases taken at 5, 25, and 65 cm intervals from the gas intake, which are shown in Fig. 215, are in reference to the maximum temperature in the oven. Only at the 5 and 25 cm interval did a range of negative temperature coefficients appear.

The oxidation of heptane took place at  $\sim 150^\circ$ , and even at  $\sim 175^\circ$  fogs were to be noted in the exhaust gases.<sup>1</sup> At the lower temperatures,

<sup>1</sup> The appearance of such fogs, sometimes accompanied by the formation of acids

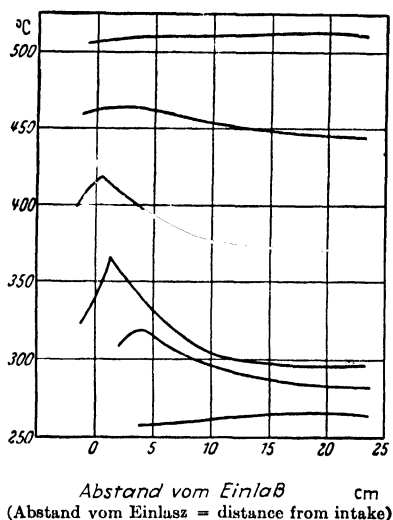
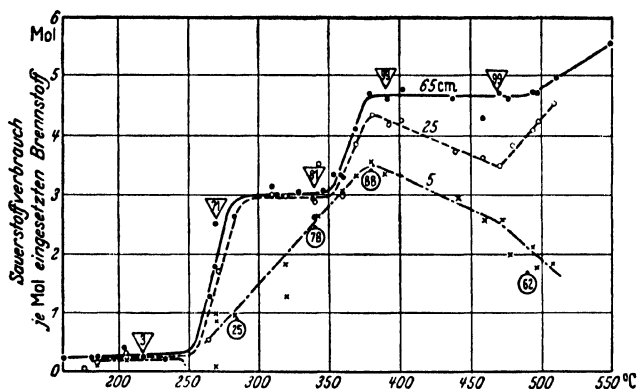


Fig. 214.—Temperature variation in the reaction chamber in the oxidation of flowing heptane-air mixtures. (From Edgar and associates, p. 447.)

it might have been a case of a heterogeneous reaction at which, to be sure, only a small percentage of the heptane is oxidized, but it is quite completely oxidized (Table 97).



(Sauerstoffverbrauch je Mol eingesetzten Brennstoff = oxygen consumed per mol of fuel used)

Fig. 215.—Oxygen consumption in the oxidation of heptane in a flow system. Oxygen consumption: x, 5 cm, o, 25 cm, •, 65 cm from the gas intake. Also plotted per cent of fuel used which is oxidized; figures in triangles, 65 cm and figures in circles, 5 cm from the gas intake. (From *Edgar and Associates*, p. 447.)

The comparison of heptane, 1-heptane, and 3-heptane (Beatty and Edgar, cited page 454) yields the following for oxidation, which might at first seem unexpected in view of the experiences of the organic chemist

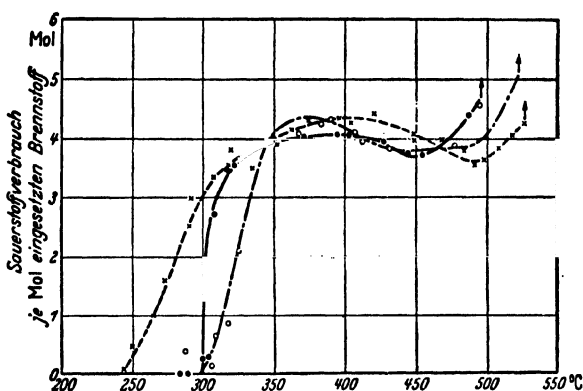
TABLE 97.—HEPTANE OXIDATION (FROM BEATTY AND EDGAR)

| Place of taking sample, cm from gas intake | Average temperature, °C | Heptane, grams |           | % of the heptane used which was oxidized | Mol of O <sub>2</sub> consumed per mol of oxidized heptane |
|--|-------------------------|----------------|-----------|--|--|
|  |                         | Amount put in  | Recovered |  |  |
| 65   | 217                     | 3.282          | 3.189     | 2.8                                      | 9.0  |
| 65   | 270                     | 3.413          | 1.008     | 70.5                                     | 3.0  |
| 65   | 340                     | 3.432          | 0.652     | 81.0                                     | 3.7  |
| 65   | 390                     | 4.0            | Trace     | 99+                                      | 4.7  |
| 65   | 470                     | 7.0            | ~ 0.05    | 99+                                      | 4.7  |
| 5  | 283                     | 5.246          | 3.957     | 24.6                                     | 4.0  |
| 5  | 343                     | 3.378          | 0.728     | 78.4                                     | 3.31   |
| 5  | 380                     | 3.764          | 0.440     | 88.3                                     | 3.96   |
| 5  | 490                     | 5.890          | 2.231     | 62.1                                     | 2.94   |

but is again and again found to be supported by observations in oxidation and in the knocking of hydrocarbons, namely, paraffin is more easily

and peroxides, is often reported. Concerning the reaction products that might be shown to be present in them, it must be considered that, in the liquid phase, drops or reactions are possible that do not come into consideration in the gas phase.

oxidized than are olefins. In the pyrex reaction chamber previously described, reaction set in at  $\sim 244^{\circ}\text{C}$  for *n*-heptane, whereas it began only at  $\sim 300^{\circ}$  for 1-heptane and 3-heptane, progressing much more rapidly in 1-heptane than in 3-heptane (Fig. 216). Beatty and Edgar conclude (a conclusion earlier arrived at by Pope, Dykstra, and Edgar for 1-octane) that the oxidation of the olefins does not begin at the double bond. In all three cases, a range of negative temperature coefficients is noted. In general, no fundamental difference exists between the oxidation of paraffin and that of the olefins even though quantitative differences appear. Both the investigation of the static temperature distribution along the oven and the taking of samples at various distances from the gas intake showed that heptane reacts closer to the gas intake than 1-heptane and that 1-heptane reacts closer than 3-heptane.



(Sauerstoffverbrauch je Mol eingesetzten Brennstoff = oxygen consumption per mol of fuel used)  
 FIG. 216.—Oxidation of — *n*-heptane; - - - 1-heptane; and - · - · 3-heptane in a flow system. (From Beatty and Edgar, p. 454.)

A more careful investigation also showed a smaller oxidation for iso-octane from  $250^{\circ}\text{C}$  on; this is probably the result of a wall reaction.

Mixtures of heptane-iso-octane (1:1 and 1:3) showed a course of reaction analogous to pure heptane, except that the temperatures of the beginning of the reaction were moved upward by  $\sim 10^{\circ}$  to  $20^{\circ}$  in comparison with the latter. The oxygen consumption is smaller with these mixtures than with pure heptane (if the latter is present in a concentration equal to the sum of the hydrocarbons) but essentially higher than would correspond to the oxidation of the heptane alone contained in the mixture, a proof that the oxidation of iso-octane is induced by the heptane oxidation.

An analysis of the mixture 1:1 showed that at  $375^{\circ}$  only 12 per cent of the fuel had remained unoxidized; *i.e.*, in a temperature range in which iso-octane alone would hardly react, the greater part of the iso-octane

TABLE 98.—OXIDIZED PORTION OF THE COMPONENTS IN AN *n*-HEPTANE-ISO-OCTANE MIXTURE 1:3 (FROM BEATTY AND EDGAR)

| Oven temperature, °C.....                                     | 383                      | 383       | 303         | 462         |
|---|--------------------------|-----------|-------------|-------------|
| Limits of the reaction zone, cm<br>from the gas intake.....   | 0-5                      | 5-65      | 0-65        | 0-65        |
| Mol % oxidized { heptane.....                                 | 73.2                     | 13.0      | 86.2        | 95.9        |
| of the { iso-octane.....                                      | 53.7                     | 16.0      | 69.7        | 84.3        |
| { total used.....   | 59.0 (88.3) <sup>1</sup> | 15.2 (11) | 74.2 (99+)  | 87.5 (99+)  |
| Mols $\frac{\text{iso-octane}}{\text{heptane}}$ oxidized..... | 1.95                     | 3.28      | 2.15        | 2.33        |
| Oxygen consumption, mols per<br>mol of oxidized hydrocarbon.  | 3.41 (3.96)              | —         | 3.39 (4.70) | 3.45 (4.70) |

<sup>1</sup> Values in parentheses for pure *n*-heptane, for comparison.

had experienced a partial, induced oxidation. In this case, about 2.6 mols of oxygen were consumed per mol of oxidized fuel. At 490°, 9 per cent of the hydrocarbons still survived, and the oxygen consumption amounted to  $\sim 3.1$  mol per mol of oxidized fuel. In addition to an induction of the iso-octane oxidation by *n*-heptane, the experimental results, especially in high iso-octane concentrations, also suggest an inhibition of the heptane oxidation by iso-octane, with which fact the discovered knock behavior of the mixtures would also agree (*cf.* Chap. XII).

Mardles<sup>1</sup> had already found that the oxidation of hexane, pentane, and pentene is inhibited by benzol, which then goes over into phenol at temperatures at which benzol alone would be stable toward oxygen.

Taking heptane as an example, Beatty and Edgar (cited page 454) observed a series of peculiarities in luminescence also.<sup>2</sup> A diffuse illumination appeared from  $\sim 250^\circ\text{C}$  on and increased in intensity with the temperature until at  $\sim 270^\circ$  a ring of blue-white "cold flame" formed at about 15 cm distance from the gas intake. From there, divided into two flame fronts, it slowly progressed in both directions in the tube and was finally extinguished. Then the same thing is repeated, at first at intervals of 10 to 12 sec, until at  $\sim 300^\circ$  the cold flames become continuous, forming a narrow zone of brighter illumination in the neighborhood of the gas intake. This place coincides with that of the maximum temperature in the tube (*cf.* page 445). At still greater increases in the temperature, the luminous zone becomes more diffuse and finally fills the tube with a diffuse illumination, again completely parallel with

<sup>1</sup> GILL, MARDLES, and TETT, *Trans. Faraday Soc.*, **24**, 574 (1928). MARDLES, *Trans. Faraday Soc.*, **27**, 681 (1931). BRUNNER, *Helv. Chim. Acta*, **13**, 197 (1930).

<sup>2</sup> On the appearance of luminescence in auto-oxidation reactions, *cf.* also Milas, *Chem. Rev.*, **10**, 328 (1932).

the temperature distribution in the tube. Further, this transition corresponds to the range of negative temperature coefficients. At 525°, ignition sets in, again about 15 cm from the gas intake.

Surfaces of rough or smooth pyrex glass, copper, copper netting, and iron had no influence on the phenomena in the reaction zone. Also considerable variations in the ratio  $O_2:N_2$ :fuel led to no fundamental changes in the phenomena.

Experiments were also carried out in a vertical oven. The fuel was dropped in from above in a liquid form. Below 300°, the dropping was followed by a luminous trace; and, at higher temperatures, the illumination appeared simultaneously with the dropping.

3-heptane showed all these phenomena more weakly.

The ringlike structure of the cold flame (as opposed to luminescence and to the usual flames at higher temperature) suggests the influence of surface effects.<sup>1</sup>

Other observations on the oxidation behavior of higher hydrocarbons are completely compatible with the conclusions of Edgar and his associates. Dumanois and Mondain-Monval<sup>2</sup> have investigated the oxidation of pentane-air mixtures at an initial pressure of 5.5 atm with progressive heating. They obtained explosion in this case at 230°. It is not surprising that, in the temperature range at which otherwise barely perceptible reaction and luminescence would set in, ignition occurs as the result of a rise in pressure.

Callendar<sup>3</sup> was the first to investigate the oxidation of a large number of hydrocarbons in a flow system. He determined the temperatures at the beginning of a perceptible conversion. As in Edgar's and Prettre's investigations, the order in which they appear corresponds to their increasing knock resistance. Callendar also analyzed the reaction products. White fogs appeared in the terminal gases of the reaction at moderately high temperatures. Peroxidic substances were also shown to be present, and this led Callendar to his peroxidation theory and the theory of the liquid reaction centers (*cf.* page 569). Table 99 shows the sequence of oxidizability found by Callendar with the high temperatures of the beginning combustion. The presence of peroxides in the reaction products, especially in the neighborhood of 300°, if white fogs simultaneously appear in the exhaust gases, has been demonstrated

<sup>1</sup> *Cf., e.g.,* PRETTRE, M., *Compt. rend.*, **207**, 532 (1938).

<sup>2</sup> DUMANOIS, P., and P. MONDAIN-MONVAL, *Compt. rend.*, **187**, 892 (1928); *Ann. Office nat. des combust. liquides*, **3**, 761 (1928). MONDAIN-MONVAL, P., and B. QUANQUIN, *Compt. rend.*, **189**, 917 (1929); **191**, 299 (1930). MONDAIN-MONVAL and WEL-LARD, *Compt. rend.*, **196**, 1226 (1933); **200**, 232 (1935). *Cf. also* ST. LEWIS, J., *J. Chem. Soc.*, 1927, p. 1555; 1929, p. 759; 1930, pp. 58, 2241.

<sup>3</sup> CALLENDAR, H.L., *Engineering*, **123**, 147, 182, 210 (1927).

TABLE 99

| Material  | <i>n</i> -Pen-<br>tane,<br>°C | Iso-<br>pen-<br>tane,<br>°C | <i>n</i> -He-<br>xane,<br>°C | <i>n</i> -Oc-<br>tane,<br>°C | No-<br>nane,<br>°C | De-<br>cane,<br>°C | Unde-<br>cane,<br>°C | Ben-<br>zol,<br>°C | To-<br>luol,<br>°C |
|---|-------------------------------|-----------------------------|------------------------------|------------------------------|--------------------|--------------------|----------------------|--------------------|--------------------|
| Temperature of<br>the beginning<br>combustion . . . | 295                           | 303                         | 265                          | 215                          | 210                | 210                | 205                  | 670                | 550                |

repeatedly,<sup>1</sup> also under conditions of engine operation.<sup>2</sup> According to Ivanov,<sup>3</sup> up to 6.5 grams of a raw peroxide was produced from 25.5 grams of cyclohexane in the oxidation of cyclohexane in the gas phase between 316° and 370°.

It is difficult to say what role the peroxides found to be present actually play in the reaction. Even though the coinciding of the range of lively reaction with the appearance of peroxides might not be accidental, it is nevertheless quite possible that the provable, stable peroxides are not themselves responsible for the reaction but rather that more unstable intermediary products are responsible.

*The Role of Peroxides in Hydrocarbon Oxidation.*—The best way to clarify this problem might be to study the behavior of the peroxides in the gas phase. Besides a number of observations on the shortening of the induction period as well as the inducing of knocking in the engine by peroxide additions only, systematic studies of recent date are available on this subject. Of these, a work by Harris and Egerton<sup>4</sup> must be discussed in greater detail.

The thermal disintegration of diethyl peroxide,  $C_2H_5-O-O-C_2H_5$ , takes place, according to Harris and Egerton,<sup>4</sup> between 130° and 190° monomolecularly and unin-

<sup>1</sup> MOUREU, C., C. DUFRAISSE, and R. CHAUX, *Chim. et ind.*, **18**, 3 (1927); *Ann. Office nat. des combust. liquides*, **2**, 238 (1927); *Compt. rend.*, **184**, 413 (1927). BENNET and E.W.J. MARDLES, *J. Chem. Soc.*, **127**, 3155 (1927). MARDLES, *Trans. Faraday Soc.*, **27**, 681 (1931). BERL, E., K. HEISE, and K. WINNACKER, *Z. physik. Chem.*, Sec. A, **139**, 453 (1928). BERL and WINNACKER, *Z. physik. Chem.*, Sec. A, **145**, 161 (1929); **148**, 36, 261 (1930). RIDEAL, E.K., and M. BRUNNER, *J. Chem. Soc.*, 1928, pp. 1162, 2824. BRUNNER, M., *Helv. Chim. Acta*, **10**, 707 (1927); **11**, 881 (1928); **13**, 197 (1930).

<sup>2</sup> DUMANOIS, P., P. MONDAIN-MONVAL, and B. QUANQUIN, *Compt. rend.*, **192**, 486 (1931); the especially careful investigations of Egerton in this field will be discussed in Chap. XII, pp. 539ff.

<sup>3</sup> IVANOV, K.I., *J. Gen. USSR*, **6**, 470 (1936). ELLIS, C., "Chemistry of Petroleum Derivatives," Vol. II, New York, 1937.

<sup>4</sup> HARRIS, E.J., and A.C. EGERTON, *Proc. Roy. Soc. London*, A, **168**, 1 (1938). Cf. also in this connection the address of A. Egerton at the meeting of the Deutsche Akademie der Luftfahrtforschung, May, 1939, to appear in the publications of the Deutsche Akademie der Luftfahrtforschung, 1939, as well as Neumann and Tutakin, *Acta Physicochim. URSS*, **9**, 861 (1938), and Aivazov, Neumann, and Chanova; *Acta Physicochim. URSS*, **9**, 767 (1938).

fluenced by the surface (packing with quartz and coating with NaCl were without influence) or by the presence of dilutions (He up to 65 per cent, H<sub>2</sub> or CO<sub>2</sub>). According to this, the reaction is therefore homogeneous and apparently not a chain reaction, even though NO lengthens the induction period that is present in any case. Down to 2 mm of pressure, no decrease in the velocity constant was to be noted. For the velocity of the nonexplosive disintegration, the following is valid ( $k$  in sec<sup>-1</sup>):

$$\log k = -\frac{6890}{T} + 14.71$$

with an apparent activation energy of 31.5 kcal. Above a critical pressure limit, explosion is obtained. In a quartz chamber, the following was valid for the critical explosion limit  $p_{\text{cr}}$  in cm Hg:

$$\log p_{\text{cr}} = \frac{5142}{T} - 10.91$$

The position of the limit depends greatly upon the diameter of the chamber but is only little raised by the addition of H<sub>2</sub> or He. For a different reaction chamber, not only the position of the limit was changed but also the apparent activation energy of 23.5 had changed from 23.5 to 15.1 kcal, a sign that a simple process is hardly responsible for the explosive disintegration.

The following were obtained as gaseous reaction products of slow disintegration at 143°C: 4.7 per cent CO<sub>2</sub>, 55.6 per cent CO, 19.4 per cent CH<sub>4</sub>, 19.4 per cent C<sub>2</sub>H<sub>6</sub>, only a trace of O<sub>2</sub>, and no unsaturated.

If diethyl peroxide was led through a tube with CO<sub>2</sub> at higher temperatures, reaction products as shown in Table 100 were obtained. The third experiment took a variant course and corresponded to disintegration above the critical limit:

TABLE 100

| Temperature, °C | Converted (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O <sub>2</sub> | HCHO | CH <sub>3</sub> CHO | C <sub>2</sub> H <sub>5</sub> OH | CO  | H <sub>2</sub> | CH <sub>4</sub> | C <sub>2</sub> H <sub>6</sub> |
|-----------------|--|------|---------------------|----------------------------------|-----|----------------|-----------------|-------------------------------|
| 187             | 8.65   | 1.9  | 3.2                 | 7.5                              | 4.7 | Trace          | 2.7             | 2.3                           |
| 201             | 17.4   | 3.9  | 6.9                 | 14.2                             | 9.8 | 1.1            | 5.9             | 3.9                           |
| 245             | 28.4   | 16.8 | 7.9                 | 10.4                             | 6.5 | 0.4            | 7.8             | 7.4                           |

For the disintegration mechanism, we refer to the original as well as to Barak.<sup>1</sup> A primary disintegration into radicals would seem quite probable, although it would then be difficult to understand that no signs of chain reactions are observed, except perhaps in the position of the explosion limits.

A bluish luminescence may be observed in the explosion, and at higher pressures a clicking is also audible. Induction periods longer than 1 sec were never observed. Air retarded the disintegration of diethyl peroxide. At higher temperatures, diethyl peroxide-air mixtures ignite at 10 cm Hg in the following manner:

|                      |     |       |       |       |
|----------------------|-----|-------|-------|-------|
| With % peroxide..... | 11  | 3.5   | 1.6   | 0.9   |
| At °C.....           | 200 | 230.0 | 260.0 | 280.0 |

<sup>1</sup> BARAK, H., and D.W.G. STYLE, *Nature*, **135**, 307 (1935).



If, instead of air, a propane-oxygen mixture 1:1 was used, likewise at 10 cm Hg, the ignition temperature of the peroxide rises:

|                                   |       |       |     |       |       |       |
|-----------------------------------|-------|-------|-----|-------|-------|-------|
| Pressure of the peroxide, cm Hg.. | 2.1   | 1.4   | 1   | 0.5   | 0.15  | 0.05  |
| Ignition, °C.....                 | 190.0 | 200.0 | 211 | 232.0 | 290.0 | 325.0 |

At the lowest pressure, a bluish luminescence is visible but no further flame or combustion. Under these conditions, propane itself does not ignite; and, even at the higher temperatures, propane shows no signs of oxidation until several minutes after the ignition of the peroxide. The conclusions do not agree with those of Neumann and Tutakin,<sup>1</sup> according to which butane-oxygen mixtures ignite and yield cold flames at the same limit pressure of the peroxide at which the latter explodes alone.

It is remarkable that, in the same reaction chamber, the same apparent activation energies for the temperature dependence of the limit pressures of peroxide are found for the explosion of diethyl peroxide (a) alone, (b) in mixture with air, and (c) with oxygen-propane 1:1, namely,

$$(a) \quad \log p = \frac{15,140}{RT} - 14.97$$

$$(b) \quad \log p = \frac{16,300}{RT} - 17.3$$

$$(c) \quad \log p = \frac{14,850}{RT} - 15.4$$

The observations of Egerton that peroxides can explode without igniting the rest of the mixture permit an easy explanation of the frequently reported findings that several cold flames can follow one another in the same mixture. The induction periods of propane oxidation are greatly shortened by diethyl peroxides in concentration of several tenths per cent, *e.g.*, from  $\sim 250$  to  $< 10$  sec.

*Further Investigations on the Oxidation of Hydrocarbons.*—Estradère<sup>2</sup> has investigated the oxidation of a series of hydrocarbons in mixture with oxygen, determining the gaseous reaction products in dependence on the temperature and making analyses of aldehydes, peroxides, and unsaturated reaction products. She used a flow apparatus with a relatively narrow, packed pyrex reaction tube because the reaction with oxygen would otherwise have been too violent. The curves obtained therefore do not yield as much detail as those of Edgar and his associates, but the sequence of the temperatures of the beginning of lively reaction agrees well with that of Edgar, insofar as the data for comparison are available, and reproduces, by and large, the sequence of increasing knock resistance.

The peroxide analyses showed, in general, a quantity of peroxides which at first increased with a rise in temperature but then disappeared

<sup>1</sup> NEUMANN, M., and TUTAKIN, *Compt. rend.*, **205**, 278 (1937).

<sup>2</sup> ESTRADÈRE, SUZANNE, *Ann. Office nat. des combust. liquides*, **8**, 484 (1933); *Pub. sci. tech. ministère air France*, No. 49, Paris, 1934; *Compt. rend.*, **202**, 217 (1936); **204**, 46 (1937).

TEMPERATURES OF THE BEGINNING OF LIVELY REACTION (FROM ESTRADÈRE)  
For hydrocarbons in Stoichiometric Mixture with Oxygen

|                               |       |                     |       |
|-------------------------------|-------|---------------------|-------|
| <i>n</i> -Pentane.....        | 360°C |                     |       |
| <i>n</i> -Hexane.....         | 318°C | 1-Hexene.....       | 370°C |
| <i>n</i> -Heptane.....        | 300°C | 1-Heptene.....      | 320°C |
|                               |       | 1-Heptine.....      | 355°C |
| <i>n</i> -Octane.....         | 292°C |                     |       |
| Iso-octane <sup>1</sup> ..... | 500°C |                     |       |
| <i>n</i> -Nonane.....         | 276°C |                     |       |
| <i>n</i> -Dodecane.....       | 260°C |                     |       |
| <i>n</i> -Tetradecane.....    | 247°C |                     |       |
| Cyclohexane.....              | 345°C | Cyclohexene.....    | 410°C |
|                               |       | Cyclohexadiene..... | 355°C |
| Methyl cyclohexane.....       | 340°C |                     |       |

<sup>1</sup> 2,2,4-trimethyl pentane.

again at very high temperatures. For other details, we must refer to the original. It is interesting to note that peroxides appeared as well with saturated as with unsaturated hydrocarbons, even with iso-octane, but that they are completely lacking in the case of benzol. This fits in the framework of all other observations on aromatics.

Where experiments were made,<sup>1</sup> it was shown that the reactionability was greatly increased by raising the hydrocarbon concentration, in other words, that the temperature of the beginning of lively reaction was correspondingly reduced, whereas conversely antiknock additions—lead tetraethyl<sup>2</sup> in small amounts and benzol in larger amounts—raise the temperature of beginning lively reaction.

Experiments carried out in a static apparatus with a reaction chamber 6 cm in diameter by Jost, v. Müffling, and Rohrmann<sup>2</sup> clearly showed in the case of *n*-heptane the influence of the composition of the mixture on the reactionability (Fig. 217). The more super-rich the mixture the clearer is the “negative temperature coefficient.” The entire course of the reaction shows that we are not dealing in this case with a reaction proceeding according to any kind of simple order but rather with a degenerate explosion. The maxima observed in the neighborhood of 250° in super-rich mixtures correspond to explosion-like pressure increases that appear after a longer induction period, whereas the same mixtures react completely quietly at higher temperatures up to about 460°.

<sup>1</sup> For example, ST. LEWIS, J., cited p. 461.

<sup>2</sup> For example, PRETTRE, M., cited p. 437. EGERTON, A.C., and L.M. PIDGEON, *J. Chem. Soc.*, 1932, pp. 66, 676. EGERTON and S.F. GATES, *Proc. Roy. Soc. London*, A, **114**, 149 (1927). MOUREU, DUFRAISSE, and CHAUX, cited p. 462. CALLENDAR, cited p. 461. LEWIS, cited p. 461. DUMANOIS, MONDAIN-MONVAL, and QUANQUIN, cited p. 462. JOST, W., and L. v. MÜFFLING, and W. ROHRMANN, *Z. Elektrochem.*, **42**, 488 (1936).

From these findings, it is likewise not surprising that regular ignition can take place at somewhat higher pressures below 250°C (page 461). In the case of the explosion-like pressure increase at low temperatures, CO and H<sub>2</sub> were shown to be present among the reaction products in great quantities; whereas, with quiet reaction, chiefly aldehydes and apparently H<sub>2</sub>CO were present instead (it must be concluded from the fact that the observed band spectrum corresponds to formaldehyde that formaldehyde appears in the range of cold flames). The relative oxidizability of *n*-heptane, *n*-hexane, ethanol, di-isobutylene, cyclohexane,<sup>1</sup> iso-octane, and benzol, as well as of a mixture 1:1 of heptane and di-isobutylene, can be seen from Figs. 218 and 219 (cf. also Fig. 213 from Pope, Dykstra, and Edgar).

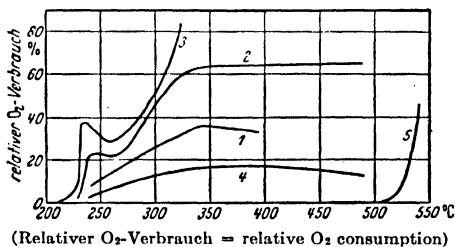


FIG. 217.—Conversion of heptano-air mixtures with 1-min reaction duration: 1, stoichiometric mixture; 2-2 x stoichiometric; 3-3 x stoichiometric; 4- $\frac{1}{2}$  stoichiometric; 5-stoichiometric iso-octane-air mixture. (From Jost, v. Müßling, and Rohrmann, p. 465.)

The following is of special interest in the oxidation of the *n*-heptane-di-isobutylene mixture (Fig. 218). As a comparison with the curves for pure heptane and pure di-isobutylene show, the heptane oxidation is greatly inhibited by di-isobutylene up to about 300°; a noticeable oxygen consumption sets in only about 50° higher than with pure heptane. On the other hand, the oxidation of di-isobutylene is also induced by heptane at higher temperatures, upward of about 350°, analogous to the experiments of Edgar and his associates on heptane-iso-octane mixtures; for, in this temperature range, the oxygen consumption is greater than would correspond to the participation of heptane. Both effects—inhibition of heptane oxidation below 300° and induction of the di-isobutylene oxidation above 350°—might result from the same process; for, if the inhibition by di-isobutylene is based on a chain-breaking reaction in which the di-isobutylene is itself oxidized, an oxidation of di-isobutylene must be coupled with the inhibition of the heptane oxidation. That sort of thing is known. Benzol, for example, which at

<sup>1</sup> For the oxidation of naphthalenes, cf. also P. Dupont, *Bull. soc. chim. Belg.*, **43**, 537 (1937). MARDLES, E.W.J., *J. Chem. Soc.*, 1928, p. 872; *Trans. Faraday Soc.*, **27**, 681 (1931). Also BERL and WINNACKER, cited p. 462. LEWIN, I., *Bull. soc. chim. Belg.*, **42**, 141 (1933).

low temperatures suppresses the oxidation and luminescence of hydrocarbons like hexane, oxidizes itself in the process (Gill, Mardles, and Tett, cited page 460). The chain-breaking effect of olefins, which is also known for thermal disintegration<sup>1</sup> and which we shall again and again be compelled to adduce in order to explain the phenomena observed in oxidation and knocking, is shown also in the fact that the oxidation

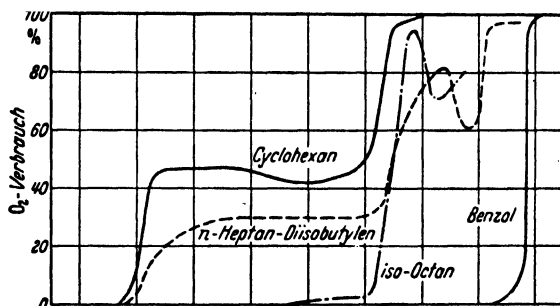


FIG. 218.  
(O<sub>2</sub>-Verbrauch = O<sub>2</sub> consumption)

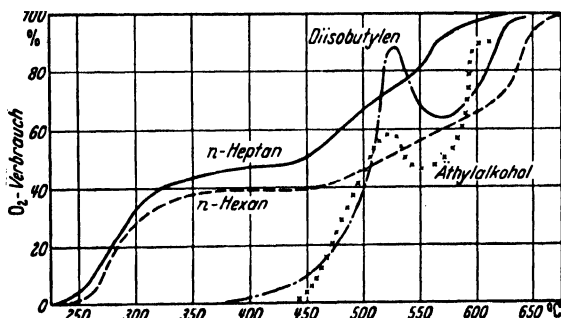


FIG. 219.  
(Äthylalkohol = ethyl-alcohol)

FIGS. 218 and 219.—Reaction of stoichiometric mixtures with air; reaction volume 130 cm<sup>3</sup>, flow velocity 10 L/hour. (From Jost, v. Müffling, and Rohrmann, p. 458.)

of aldehydes<sup>2</sup> like acetaldehyde and benzaldehyde is inhibited by octene. In this case too, the octene itself is oxidized.

The oxidation of aromatic hydrocarbons has not been investigated so extensively as has that of the aliphates. It is clear from earlier remarks (page 438) that benzol hydrocarbons do not show the phenomena of the cold flames, are generally considerably more difficult to oxidize than all other groups of organic substances (benzol is also more difficult than iso-octane; cf. Fig. 218, from Jost, v. Müffling, and Rohrmann),

<sup>1</sup> RICE, F.O., and O.L. POLLY, *J. Chem. Phys.*, **6**, 273 (1938).

<sup>2</sup> FIGULEVSKII, V.V., *J. Gen. Chem. USSR*, **4**, 616 (1934), from C. Ellis, "The Chemistry of Petroleum Derivatives," Vol. II, New York, 1937.

and in addition can inhibit the oxidation of other substances and suppress luminescence (Prettre). The kinetics of benzol oxidation were investigated in greater detail by Hinshelwood and Fort<sup>1</sup> as well as by Amiel.<sup>2</sup>

The kinetics of benzol oxidation show no essential differences from those of the other hydrocarbons. Hinshelwood and Fort observed a completely analogous course, with induction period, *e.g.*, in methane. The reaction is likewise of a higher order in respect to the hydrocarbon. The apparent heat of activation of benzol oxidation is higher than that

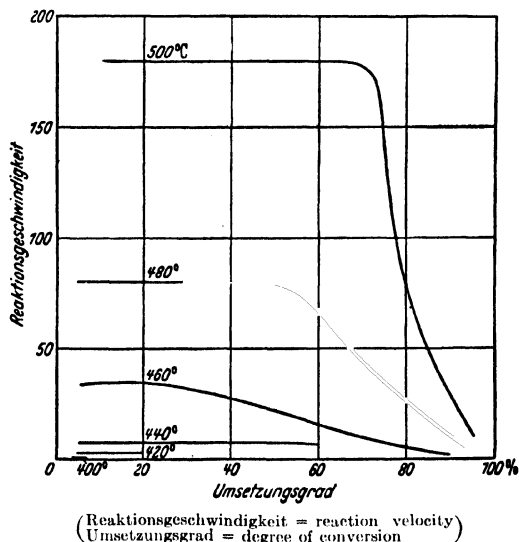


FIG. 220.—Reaction velocity (compare text) in the oxidation of benzol in stoichiometric mixture with oxygen at atmospheric pressure. (From Amiel, p. 460.)

of paraffinic hydrocarbons (with the exception of methane). From Hinshelwood's experiments, we can compute  $\sim 50$  kcal; Amiel obtained  $\sim 56$  kcal.

Amiel has made very careful measurements in a temperature range of 400° to 564°C. For purposes of orientation, we present in Fig. 220 (from Amiel) reaction velocities (percentage of carbon that is converted into CO and CO<sub>2</sub> per hour) as functions of the converted benzol for various temperatures. The reaction velocity quickly reaches a maximum value,  $w$ , which remains constant over a wide range.  $w$  is represented by

$$\log w = -\frac{12,300}{T} + 18.22$$

<sup>1</sup> HINSHELWOOD, C.N., and FORT, *Proc. Roy. Soc. London, A*, **127**, 218 (1930).

<sup>2</sup> AMIEL, J., *Compt. rend.*, **196**, 1122, 1899 (1933); **197**, 984 (1933); *Ann. chim.*, (11), **7**, 70 (1937); extensive bibliography.

The oxidation of aromatic hydrocarbons—benzol, toluol, and ethyl benzol—at high pressures and relatively low temperatures has been investigated by Newitt and Burgoyne.<sup>1</sup>

In the oxidation of *benzol* under pressures up to 50 atm, up to 50 per cent of the benzol consumed can be obtained as phenol.<sup>2</sup> In this respect, then, aromatic hydrocarbons completely follow the behavior of the aliphatic hydrocarbons. The phenol yield is higher, the higher the ratio benzol:oxygen; and, even if flame formation sets in, a part of the phenol still survives. At these high pressures, the benzol oxidation had already set in with notable velocity from 280° on, and it appeared without a marked induction period.

The order of magnitude of the reaction velocity can be obtained from Table 101, which refers to mixtures of 1.5 hydrocarbon:1 oxygen at an undefined pressure.

TABLE 101

| Material          | Temperature,<br>°C | Duration of the     |                    |
|-------------------|--------------------|---------------------|--------------------|
|                   |                    | Induction<br>period | Reaction<br>period |
|                   |                    | min                 |                    |
| Benzol.....       | 293                | 0                   | 3                  |
| Toluol.....       | 251                | 6                   | 2                  |
| Ethyl benzol..... | 239                | 6                   | 2                  |

Packing of the reaction chamber with metal shavings inhibited the oxidation of benzol, to be sure, but not markedly that of toluol and ethyl benzol. Nitrogen additions always had a reaction-retarding effect. Benzol-air in the ratio 40:9.5 yielded, at 50 atm and 362°C, over 50 per cent phenol in relation to the phenol burned, in addition to the following reaction products, expressed in the relative participation of the oxygen in the products:

|                               |            |
|-------------------------------|------------|
| Phenol.....                   | 10.6       |
| Quinone and hydroquinone..... | Trace      |
| Maleic acid.....              | 2.8        |
| Formaldehyde.....             | 3.0        |
| CO.....                       | 26.2       |
| CO <sub>2</sub> .....         | 29.8       |
| H <sub>2</sub> O.....         | 27.6       |
|                               | <u>100</u> |

<sup>1</sup> NEWITT, D.M., and J.H. BURGOYNE, *Proc. Roy. Soc. London*, A, **153**, 448 (1936).

<sup>2</sup> AMIEL, *cf.* p. 468, proved phenol and quinone to be present in the reaction products at atmospheric pressure.

Maleic acid is always obtained as the most essential intermediary product in the destruction of the ring.

In *toluol*, just as in ethyl benzol, the oxygen attack takes place preponderantly at the  $\alpha$ -C-atom of the side chain. Benzyl alcohol, benzaldehyde, and under certain circumstances much benzoic acid are obtained as a product of the attack at the nucleus; in a subordinate degree, 2,4-hydroxytoluol is also obtained. The share of the oxidation in the nucleus comprises between 8 and 28 per cent of the total oxidation. The following was obtained in a mixture of 1.5 toluol + O<sub>2</sub> at 18.8 atm:

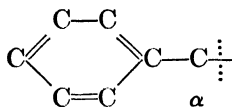
|              | Benzyl<br>alcohol | Benzal-<br>dehyde | Benzoic<br>acid | 2,4-Hy-<br>droxy-<br>toluol | CO <sub>2</sub> | CO  |
|--------------|-------------------|-------------------|-----------------|-----------------------------|-----------------|-----|
| At 216°..... | 2.6               | 18.8              | 34.4            | 5.8                         | 9.3             | 2.6 |
| At 276°..... | 1.7               | 4.9               | 1.7             | 5.4                         | 3.0             | 9.7 |

The products are expressed by the share of oxygen of the burned toluol. In the second experiment, flaming had taken place.

Raising the ratio toluol:O<sub>2</sub> raises the share of benzyl alcohol and benzaldehyde.

*Ethyl benzol* yields phenyl methyl carbinol, acetophenone, benzaldehyde, benzoic acid, and, as a result of the attack at the nucleus, 2,4-dihydroxyethyl benzol. Since it has been established in special experiments that acetophenone in oxidation yields considerable quantities of benzoic acid and benzaldehyde, these products could also in this case be formed by way of the acetophenone.

That aromatic hydrocarbons with a side chain<sup>1</sup> are attacked at the place of the  $\alpha$ -C-atom is not unexpected from the point of view of the double-bond rule that the bonds following the  $\alpha$ -C-atom correspond to



exactly the place where the disintegration of aliphatic unsaturated substances would prefer to set in. From this, it follows that it is necessary to adopt the following from Hein<sup>2</sup> as the primary step in the thermal disintegration of toluol between 900° and 1100°C, according to the

<sup>1</sup> This was first demonstrated in the liquid phase, but it is necessary for reasons mentioned before to be cautious about applying such results to the gas phase. STEPHENS, H.N., *J. Am. Chem. Soc.*, **48**, 1824 (1926); **56**, 2523 (1928); *J. Phys. Chem.*, **37**, 209 (1933).

<sup>2</sup> HEIN, F., and H.I. MESSE, *Naturwissenschaften*, **26**, 710 (1938).

method of Rice



The benzyl radicals are proved by the reaction with Hg into  $(\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{Hg})_2$ ; by itself, toluol disintegrates into dibenzyl and hydrogen.

### C. THE IGNITION OF HYDROCARBONS, ESPECIALLY AT HIGH PRESSURES

In the preceding sections, we have seen again and again what an influence the container wall can have on the individual phases of hydrocarbon oxidation. There is really only one apparatus by means of which we can free ourselves of all these influences, with the exception of the cooling effect of the wall, namely, by investigating the ignition of a hydrocarbon-air mixture by adiabatic compression (for the method, *cf.* Chap. I, pages 19, 33). If we have a container with a diameter of the order of magnitude of several centimeters and in it a gas compressed to several times its normal pressure, we estimate according to the formula of the square of displacement (*cf.* Chap. VIII, page 286) that times of the order of magnitude of 1 sec or above are necessary for the diffusion from the interior to the wall (or the reverse). On the other hand, it is shown (*cf.* page 474) that, according to this method, it is possible to obtain induction periods for auto-ignition between several  $10^{-3}$  and several  $10^{-1}$  sec. In these periods, no considerable diffusion from the interior to the wall or the reverse can yet have taken place. To be sure, an exchange has already taken place by diffusion between the parts close to the edge and the wall. The same parts have already cooled considerably during the same period, however, and for this reason hardly contribute to the real reaction. Essentially, therefore, we are actually observing the results of a homogeneous gas reaction. The fact that, according to the nature of the method, the wall must always be essentially colder (several  $100^\circ\text{C}$ ) than the gas mass is also of importance for the absence of a catalytic wall reaction under these conditions. This occasions another difficulty in the quantitative results of such experiments: During the induction period leading to auto-ignition, there is always a cooling in the reaction volume that cannot be disregarded. To be sure, the half-life period for cooling by conduction (with the exclusion of convection) is of about the same order of magnitude as that for the equalization of concentration by diffusion to the wall, *i.e.*,  $\sim 1$  sec (by the way, the experiments of Tizard and Pye, to be discussed below, bear this out directly), and the reaction time always remains noticeably below this period. Since a cooling of  $10^\circ$  has a considerable effect on the reaction velocity, however, the cooling effect can never be negligible. How the temperature, really determining for the reaction, is to be obtained, requires a very careful discussion (*cf.* also pages 534*ff.*).



The measurements of Tizard and Pye<sup>1</sup> were carried out in an engine-like experimental cylinder 75 mm in diameter with a compression stroke of 20 cm. The piston was stopped at the point of maximum compression. The cylinder itself could be heated, in the last apparatus of Tizard and Pye, up to a maximum of 180°C. The compression ratio could be fixed at  $\epsilon = 6$  or 9. The ignition and the induction period necessary for it were obtained from the simultaneously recorded indicator curve. For details of the technically interesting apparatus, we must refer to the original.<sup>2</sup> The maximum temperature obtainable in the compression can be computed from the compression ratio (in this manner, Dixon computed the ignition temperatures determined by adiabatic compression). In reality, the temperatures always lie below this point because of the cooling effect of the walls. In Tizard and Pye's experiments, for example, the compression normally lasted 0.14 sec (compression could also be somewhat more rapid, but the apparatus was then occasionally damaged on account of the great accelerations). In this compression duration, the maximum pressure was found to be between 5 and 10 per cent lower than was computed for adiabatic compression. Correspondingly, the average gas temperature therefore also lies below the computed maximum.

It is very difficult to determine accurately what the temperature in the volume element was in which ignition just took place. Tizard and Pye have established ignition under various cooling conditions without and with a fan rotating in the mixture and have attempted arithmetically to eliminate the cooling effect. Here, too, we must refer to the original.

The recorded pressure (as a measure of the average temperature) can drop as well as rise during the induction period, but probably the temperature during the induction period preceding ignition will at least not drop in those places where ignition sets in and which are distant from the wall and therefore least subject to cooling.

Whether ignition takes place or not is without influence on the recorded drop in pressure during the induction period, a sign that only an extraordinarily small conversion takes place during the greater part of the induction period. In a series of 12 experiments with octane, for example, ignition took place eight times, but the drop in pressure during the first  $\frac{1}{10}$  sec was in all cases the same.

Of interest are also the experiments with ether, in which the locking mechanism of the apparatus failed and two successive compressions took

<sup>1</sup> TIZARD, H.T., *Proc. NE Coast Inst. Engng.*, **31**, 381 (1921). TIZARD and D.R. PYE, *Phil. Mag.*, **44**, 79 (1922). TIZARD, *Trans. Faraday Soc.*, **22**, 352 (1926). TIZARD and PYE, *Phil. Mag.*, (7), **1**, 1094 (1926).

<sup>2</sup> For this and for the remaining part of this section, see also D.M. Newitt and D.T.A. Townend, "The Science of Petroleum," Vol. IV, pp. 2950ff.

place (Fig. 221). Of two analogous experiments, ignition appeared in the first with the second compression, but not in the second, although the maximum temperature in the second compression of the first experiment was lower than the maximum temperature in the first compression of the second experiment. Tizard and Pye assume that locally higher temperatures were nevertheless present. Perhaps the assumption is more reasonable that an activation by the pre-reaction in the first compression had taken place.

Figure 222 and Table 102 give a survey of the results. In Fig. 222, the induction periods of the auto-ignition are plotted for various temperatures, for ethyl ether, *n*-heptane, and carbon disulphide; the direct

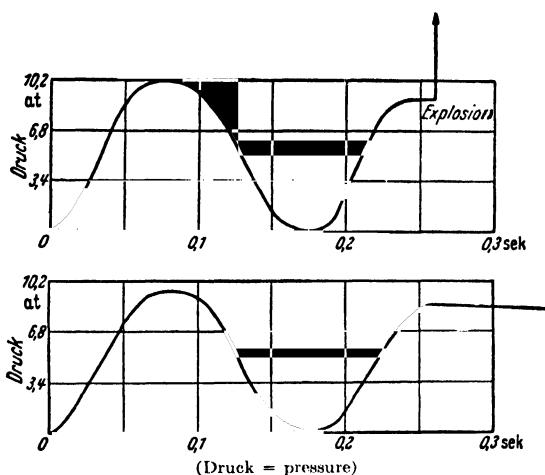


FIG. 221.

measurement values are recorded, *i.e.*, the average temperatures computed from the maximum compression pressure. The true temperatures in the interior of the gas might therefore have been somewhat higher (*cf.* page 474), the logarithms of the induction periods being plotted against the reciprocal absolute temperature. For ether and *n*-heptane, we can (disregarding the point representing the shortest induction period, assuming that this point is the most uncertain), in this figure, draw a straight line approximately through the measuring points, which leads to an apparent activation heat of about 30 to 35 kcal. The points for carbon disulphide are also added, since they show that the lowest measurable ignition temperature is lower than for *n*-heptane but that, nevertheless, ignition at higher temperatures takes place more slowly than in the latter because of the smaller temperature coefficient. From this, it is clear that the inclination to spontaneous ignition (which plays a role in the following chapter with respect to the knocking process) is not

unequivocally given for various materials by the lowest measurable ignition temperature; it is rather necessary to add at least an entity characterizing the temperature dependence.

An approximately exponential dependence of the ignition delays on the temperature (as represented by the logarithmic straight lines in Fig. 222) is to be expected for thermal explosions (*cf.* Chap. I, page 18) and (insofar as no special complications arise, *cf.* pages 490ff.) also

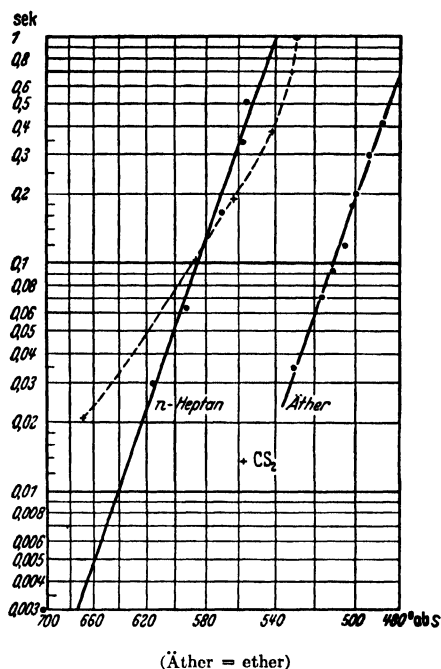


FIG. 222.—Induction periods in the ignition of various mixtures with air by adiabatic compression. Plotted are the logarithms of the ignition delays against the reciprocal absolute temperature. (*From Tizard and Pye, p. 464.*)

for chain explosions (*cf.* Chap. VIII, page 281). Taking exact account of cooling and the finite compression duration would naturally modify the activation heat obtained.

The lowest observable ignition temperatures afford a good point of departure for a comparison of similar hydrocarbons. In Table 102, we present values for these from Tizard and Pye (according to the compilation of Newitt and Townend, cited page 472). It shows average gas temperatures computed from the recorded maximum compression pressure. These temperatures will therefore again be somewhat lower than the temperature of the hottest gas portions (the difference will be smaller than 50°C; for temperatures higher by about this amount are

computed for adiabatic compressions without cooling from the compression ratio).

Experiments with various initial temperatures also exist for benzol, in other words, varied pressure with about the same terminal tempera-

TABLE 102.—LOWEST IGNITION TEMPERATURES IN ADIABATIC COMPRESSION OF HYDROCARBON-AIR MIXTURES (FROM TIZARD AND PYE)

| Material               | Mixture, parts<br>by weight of<br>fuel to 15 air | Temperature<br>before com-<br>pression, °C | Ignition<br>temperature,<br>°C |
|------------------------|--|--|--------------------------------|
| <i>n</i> -Pentane..... | 1.0  | 60   | 336                            |
| <i>n</i> -Hexane.....  | 1.0  | 60   | 306                            |
| Cyclohexane.....       | 1.0  | 60   | 324                            |
| <i>n</i> -Heptane..... | 0.8  | 59   | 291                            |
|                        | 1.6  | 59   | 292                            |
|                        | 0.4  | 13   | 292                            |
|                        | 1.0  | 40   | 284                            |
| <i>n</i> -Octane.....  | 1.0  | 60   | 275                            |
| Benzol.....            | 1.0  | 40   | 373                            |

tures. From this, it can be seen—of course, not very exactly—that a rise in pressure of 23 per cent makes about as much difference in the acceleration of the conversion as a rise in temperature of 7°, *i.e.*, the ignition delay, as could be expected, is most sensitive to a change in temperature.

In the main, the table shows the following: In the paraffin series, the lowest ignition temperature decreases with increasing chain length, corresponding to decreasing knock resistance (*cf.* Chap. XII, pages 555*ff.*). Cyclohexane ignites more slowly than hexane; benzol ignites considerably more slowly, which likewise is paralleled by the knock behavior. The experiments with variations in the composition of the mixture yield the lowest ignition temperature in about stoichiometric mixture; for variations in knock behavior with composition, *cf.* F. Seeber, cited page 592.

Recent experiments on the auto-ignition of hydrocarbons in mixture with air by adiabatic compression<sup>1</sup> are in good agreement with the results of Tizard and Pye, insofar as the same materials were investigated (Fig. 223). The experiments permit quantitative conclusions regarding the knock behavior of the investigated materials. We refer to the original work as well as to Chap. XII.

<sup>1</sup> JOST, W., and H. TEICHMANN, *Naturwissenschaften*, **27**, 318 (1939). For detailed description of the experiment and further conclusions, *cf.* W. Jost, Address at the meeting of the Deutsche Akademie der Luftfahrtforschung, May, 1939; in *Schriften deut. Akad. Luftfahrtforsch.*, 1939.

*The Experiments of Townend and Associates.*—Of interest for the kinetics of hydrocarbon oxidation and also for knock behavior are the experiments of Townend and his associates, even though they are not so free from secondary influences in respect to method as are those by Tizard and Pye. Townend and collaborators<sup>1</sup> used as their reaction chamber a steel container 15 cm in length and 4 cm in diameter which could also be lined with other material to vary the surface, and into which could be introduced the fuel-air mixture that had been prepared in a storage tank (which could be preheated). The filling required

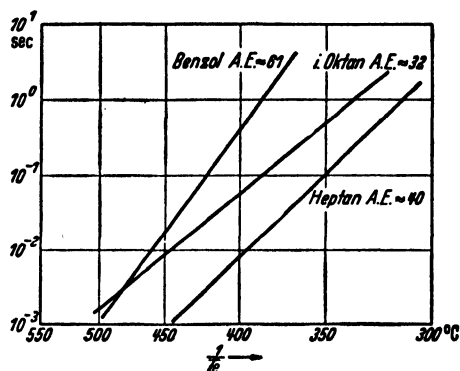


FIG. 223.—Ignition delays (logarithmically plotted) for stoichiometric mixtures of benzol, *i*-octane, and *n*-heptane with air, as well as apparent activation energy in kcal (temperatures not yet corrected from cooling). (From Jost and Teichmann, p. 475.<sup>1</sup>)

$\frac{1}{2}$  to 1 sec; reaction and explosion were determined by changes in pressure for which purpose various manometers were provided, depending on the pressure range to be investigated.

The induction periods up to ignition that were observed were situated between about  $\frac{1}{2}$  sec (comparable with the time required to admit the mixture) and a number of seconds, sometimes up to 2 hr. In the case of induction periods of minutes or even hours, it can, under chosen experimental conditions, by no means have been a matter of thermal explosion; there must, at least in the initial stage, have been an acceleration by means of chain-branching with the production of relatively stable intermediary products, at least in the longest induction periods. These

<sup>1</sup> TOWNEND, D.T.A., and M.R. MANDLEKAR, *Proc. Roy. Soc. London*, A, **141**, 484 (1933); **143**, 168 (1934). TOWNEND, L.L. COHEN, and MANDLEKAR, *Proc. Roy. Soc. London*, A, **146**, 113 (1934). TOWNEND and E.A.C. CHAMBERLAIN, *Proc. Roy. Soc. London*, A, **154**, 95 (1936); **158**, 415 (1937). KANE, G.P., and TOWNEND, *Proc. Roy. Soc., London*, A, **160**, 174 (1937). KANE, CHAMBERLAIN, and TOWNEND, *J. Chem. Soc.*, 1937, p. 436. MACORMAC, M., and TOWNEND, *J. Chem. Soc.*, 1938, p. 238. Cf. also TOWNEND, *Chem. Rev.*, **21**, 259 (1937). Also NEWITT and TOWNEND, "The Science of Petroleum," Vol. IV.

might very well be aldehydes, which might partly form at the wall, an assumption supported by the influence of aldehyde additions on induction periods observed by Townend, an influence that disappears as higher temperatures are reached. An influence of the wall on ignition behavior has been proved directly by Townend.

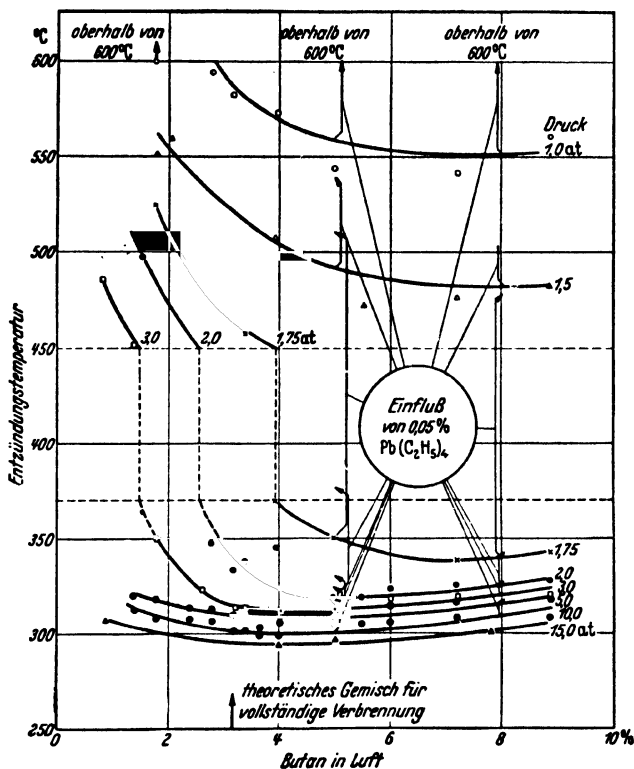


FIG. 224.—Auto-ignition of butane-air mixtures as well as the influence upon it by the addition of lead tetraethyl. (Arrows indicate the displacement of the explosion limit.) (From Townend et al., p. 468.)

Townend and his associates find as characteristic the existence of two ignition ranges, one in the neighborhood of 500° and the other in the neighborhood of about 300°C, and this agrees well with all earlier observations, especially those on cold flames. As an illustration, we give the relations for *n*-butane in Fig. 224. Here the lowest ignition temperatures for various initial pressures are plotted as the function of the composition.

of the mixture; raising the pressure and raising the fuel concentration effect a lowering of the ignition temperature, *i.e.*, under certain circumstances a transition from the upper to the lower ignition range. An addition of  $\text{Pb}(\text{eth})_4$  can have the opposite effect.<sup>1</sup> Mixtures with 5 and 8 per cent of butane and air at the pressure that was just adequate for the transition from the upper to the lower ignition range ( $1\frac{3}{4}$  atm) showed a great susceptibility to lead tetraethyl, which, mixed with butane in a concentration of 0.05 per cent, raised the ignition point by  $160^\circ$  or  $138^\circ\text{C}$ . At higher pressures, the influence was much smaller (sometimes only a few degrees centigrade).

As the cause for the transition from the lower to the upper ignition range, Townend and his associates conjecture that an easily oxidizable intermediary product can, under certain circumstances, disintegrate more rapidly or otherwise be consumed, forming materials more difficult to oxidize. Some such process might also be the cause of the negative temperature coefficient. Under certain circumstances, direct proof can be furnished for the conjecture of Townend and his associates that aldehydes, for example, can disintegrate (*e.g.*, formaldehyde to CO and  $\text{H}_2$ ) before they oxidize further.<sup>2</sup> There are, however, other possible explanations (see pages 493ff.). Phenomena like those for butane have also been observed in propane, pentane, and higher paraffins.

It was further found that the range of transition from low-temperature ignition to high-temperature ignition in general coincides with that of the appearance of cold flames. Figure 225 might serve as an example. It shows the relations in propane-air mixtures with 2.6 and 7.5 per cent of propane. In Fig. 225, the induction periods passing up to ignition are also plotted (italicized figures). In the shaded section, cold flames appear below the pressure required for normal ignition, as was determined by the pressure strokes as well as visually by means of an observation window. That in this range the appearance of cold flames and normal ignition are not independent phenomena, however, is clear from the fact that normal ignition is here always preceded by the appearance of a cold flame (in agreement with the findings of Neumann and Aivazov, Andreev, etc., *cf.* page 452).

The following materials were investigated by Townend and his associates in all: methane, ethane, propane, butane, isobutane, pentane, hexane, heptane, octane, iso-octane, ethylene, propylene,  $\alpha$ -butylene, and  $\alpha$ -amylenes; methanol, ethanol, and propanol; formaldehyde, acetaldehyde, and propionaldehyde; di-ethyl ether and di-isopropyl

<sup>1</sup> For the effect of  $\text{Pb}(\text{C}_2\text{H}_5)_4$  on ignition behavior, *cf.* A.C. Egerton and Gates, *J. Inst. Petroleum Tech.*, **13**, 244 (1927).

<sup>2</sup> *Cf.* JOST, v. MÜFFLING, and ROHRMANN, cited, p. 465; this explanation cannot be generally valid, because of the slow disintegration of the aldehydes.

ether; acetone; and benzol. A survey of the details is furnished by Figs. 226 to 236. In principle, the following might be mentioned. A decided separation into an upper and lower ignition range appears

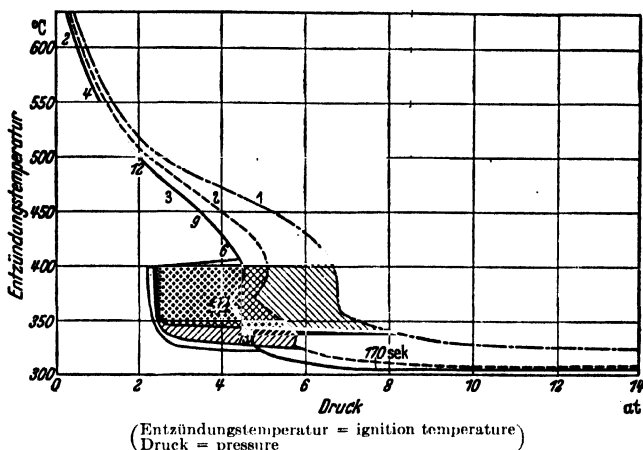


FIG. 225.—Critical explosion limits for propane-air mixtures with 2.6 per cent propane, 1; 5 per cent propane, 2; 7.5 per cent propane, 3. Range of cold flames shaded; induction periods (sec) in italicized figures. (From Townend et al., p. 468.)

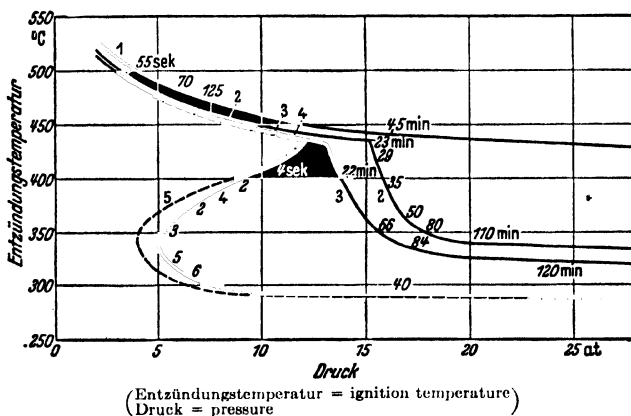


FIG. 226.—Ignition of ethane-air mixtures with (1) 6 per cent, (2) 10 per cent, (3) 13 per cent ethane; (4) and (5) as in (3) but with addition of 1 or 2 per cent acetaldehyde. Italicized numbers = ignition processes in sec or min. [From Townend et al., *Proc. Roy. Soc. London, A*, vol. 154 (1936).]

only from propane on up; in methane, no hint as to such a separation is present as yet; and, in ethane, a sharp bend appears in the pressure-temperature curve, at least for higher hydrocarbon concentrations. Figure 226 shows this and also indicates the following: At the lowest



ignition temperatures of mixtures rich in ethane, extraordinarily long induction periods appear, sometimes up to 2 hr. It can further be seen (curves 4 and 5) that an addition of small quantities of acetaldehyde (1 or 2 per cent), curves 4 and 5, causes a considerable lowering of the ignition temperature. But, and this is of special importance, acetaldehyde is effective only in the range of low temperatures (below 435°C) and long induction periods, at the same time effecting a considerable shortening of the induction period. On the one hand, this would be in agreement with the assumption that, during the induction period in the low-temperature range, a reaction mainly takes place leading to the production of aldehyde, probably more or less at the wall; and, on the other hand, it supports the explanation suggested by Townend and his associates for ignition at high temperatures—that aldehydes disintegrate<sup>1</sup> there more rapidly than they are further oxidized.<sup>2</sup> Finally, this finding leads to an easy solution of the already mentioned (page 425) discrepancy between Steacie and Plewes's and Bone and Hill's experiments, of which the first established a shortening of the induction period by acetaldehyde for ethane oxidation at 452° but no other influence on the reaction, whereas Bone and Hill were able to produce ignition in the otherwise sluggish ethane-rich mixture of 316° by means of 1 per cent of aldehyde.

As is known, the oxidizability in the sequence paraffin, alcohol, aldehyde increases for the first three members of the series. Up to propylene, the olefins are also more easily oxidized than the paraffins; but, from butylene on, the situation is reversed. The experiments of Townend and his associates thus conform to the above-mentioned rule: For paraffins, olefins, and alcohols, the oxidation stability decreases with increasing carbon-atom chain, but the decrease is less for olefins and alcohols than for paraffins; and, with increasing size of the molecule, a reversal in the oxidation behavior therefore takes place, this reversal occurring in the neighborhood of butane. Below, olefins and alcohols are less stable in oxidation than paraffins, and above, more stable than paraffins.

Under the conditions of the experiments of Townend and his collaborators, iso-octane too shows no fundamentally different behavior, except that all the phenomena occur at correspondingly higher temperatures. On the other hand, benzol shows a completely steady variation of the ignition temperatures with the pressure, without cold flames, in agree-

<sup>1</sup> But it must be remembered (p. 398) that aldehyde disintegration can be greatly accelerated by simultaneous radical chain reactions.

<sup>2</sup> For analyses of the reaction products in cold flames, cf. D.M. Newitt and Thornes, *J. Chem. Soc.*, 1937, p. 1656; see also D.M. Newitt, *J. Inst. Petroleum Tech.*, **25**, 137 (1939), especially in respect to knocking behavior.

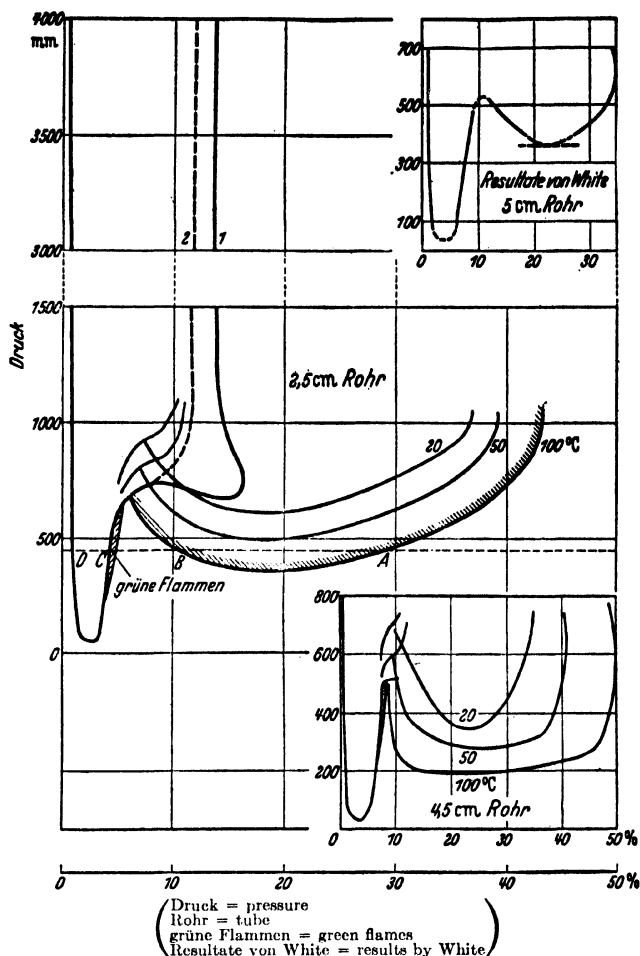


FIG. 227.—Ignition limits for ethyl ether in air for various pressures in a 2.5-cm tube. To the left, range of normal flames; to the right, range of cold flames (for various temperatures). In curve 1 the cold flame passed over into a normal flame at about  $\frac{1}{2}$  the length of the tube; curve 2 shows limits in which normal flames appeared from the start. [From Townend et al., *Proc. Roy. Soc. London*, vol. 158 (1937).]

ment with all other observations. Acetone<sup>1</sup> proves to be stable in oxidation corresponding to its high knock resistance; but, like iso-octane, it also furnishes cold flames.

<sup>1</sup> On the photochemical oxidation of acetone at  $\lambda = 3130 \text{ \AA}$  and low temperatures, which, like the disintegration, takes place with a quantum yield of 0.24, cf. P. Fugassi, *J. Am. Chem. Soc.*, **59**, 2092 (1937); on photochemical disintegration (at  $3130 \text{ \AA}$ ), cf. Dawson and Daniels, *J. Am. Chem. Soc.*, **55**, 2363 (1933).

Peculiar, too, is the behavior of the ethers. White<sup>1</sup> found that there are two ignition ranges at low pressures (as a function of the mixture composition for ignition), of which one corresponds to ordinary flames and the other corresponds to cold flames. For ordinary flames, a spark was used and, for cold flames, a heated platinum spiral was necessary. It is noteworthy that cold flames may also be induced by ignition from one point in *cold* mixtures.<sup>2</sup> Townend and Chamberlain have investigated these relations in greater detail and have obtained the results

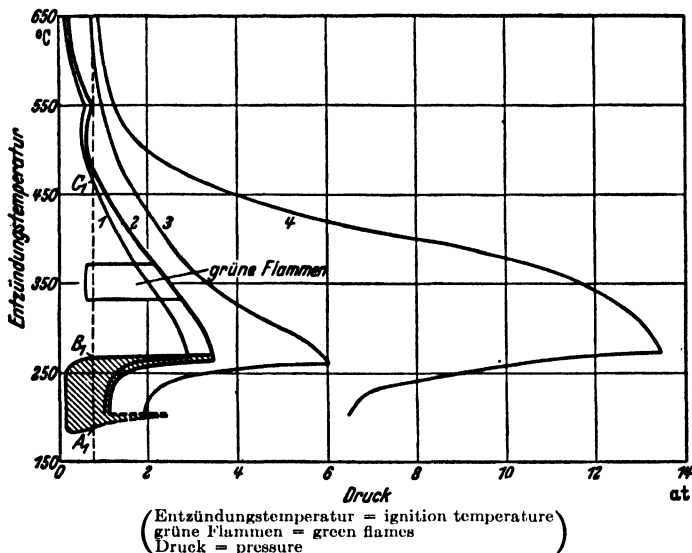


FIG. 228.—Ignition of ether-air mixtures; (1) 10 per cent, (2) 5 per cent, (3) 2 per cent, (4) 1 per cent ether. Shaded portion is the range of cold flames for 5 per cent ether in air. [From Townend et al., *Proc. Roy. Soc. London*, vol. 158 (1937).]

shown in Fig. 227. They worked with a heated tube 2.5 cm in diameter and 1 m long. Ignition took place by means of a spark or a glowing platinum spiral. The spark is not capable of igniting cold flames, just as conversely the platinum spiral yields only a superficial combustion in the range of normal flames (*cf.* Chap. I, pages 22ff.). In this case, as is customary, ignition was regarded as such only if the combustion had traversed the entire tube. Passage over into a wider tube (4.5 cm in diameter) extended the ignition limits.

The velocity of the cold flames in the 4.5-cm tube was, independent of the pressure (between 240 and 700 mm Hg) and of the temperature (between 20° and 160°C), about 24 cm/sec; in the 2.5 cm tube, it amounted to only 13.5 cm/sec.

<sup>1</sup> WHITE, A.G., *J. Chem. Soc.*, 1927, p. 498, and earlier works.

<sup>2</sup> TOWNEND and HSIEH (*J. Chem. Soc.*, 1939, pp. 332, 337, 341) have since been able to do this also with paraffin hydrocarbons.

Further, in the case of ether-air mixtures, ignition temperatures were obtained as a function of the pressure (Fig. 228); they show many similarities with the conditions in hydrocarbons. It is striking that not only is a range of cold flames obtained between 180° and 270°C for fuel-rich mixtures but that between 230° and 365° a range of green flames (in which the Swan bands predominate) exists that are identical neither with the bluish cold flames nor with the white or yellowish normal flames. In addition, an irregularity in the pressure-ignition temperature variation appears in the case of rich mixtures in the neighborhood of 500°. The extremely low position of the lowest ignition temperature again parallels the small knock resistance of ethyl ether.

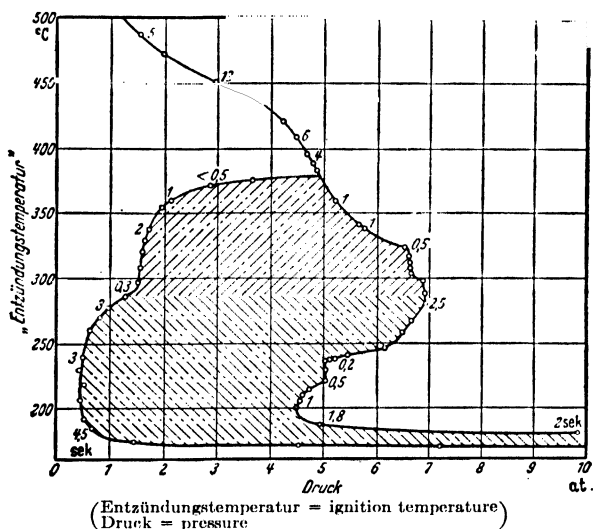


FIG. 229.—Ignition of di-isopropyl ether-air mixtures with 2.5 per cent content. Range of cold flames is shaded. Ignition delays given in sec. [From Townend et al., *J. Chem. Soc.* (1938).]

Di-isopropyl ether (Fig. 229) shows, as a whole, a behavior similar to that of ethyl ether with a similarly situated lowest ignition temperature, but at higher pressures. This is perhaps remarkable in view of the very high knock resistance of di-isopropyl ether. Townend and his associates point to the following: The range of cold flames that extended from 390° downward seemed to be of a composite nature. In the lower range of the cold flames, the induction periods dropped with the temperatures; above it, the induction periods at first rose abruptly and then dropped again. In addition, the cold flames seemed to be blue at pressures above 3 atm in the upper system and of less intensity than in the lower system, where they are more purple and more intense. For regular ignition, minima likewise appear in the induction periods, being located

at  $\sim 240^\circ$  and  $320^\circ$ . Furthermore, the explosions following the cold flames in the lower range were more violent by far. The parallel of the two separated ranges of cold flames in ethyl ether suggests itself. It is suspected that the primary oxidation of ether is determining for the low-temperature range and that the primary oxidation of one of the intermediary products analogous to hydrocarbon oxidation, *e.g.*, acetaldehyde, is determining for the range of higher temperatures. The lowest pres-

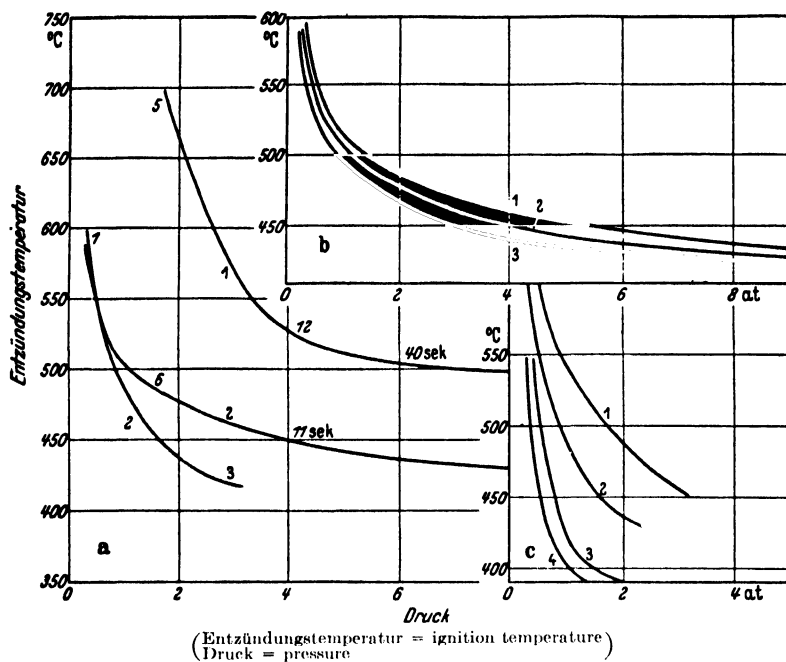


FIG. 230.—a is the ignition of 10 per cent ethane in air (1) and corresponding mixture with methanol (2) and formaldehyde (3). Italicized figures = induction periods in sec. b is the ignition of (1) 8 per cent, (2) 12 per cent, and (3) 18 per cent methanol in air. c is the same for 8 per cent formaldehyde (1) and 16 per cent formaldehyde (2) in air or the same quantities in oxygen (3) and (4). [From Townend *et al.*, *J. Chem. Soc.* (1937).]

sure necessary for ignition at low temperatures is essentially higher for isopropyl ether than for ethyl ether, which, according to Townend, explains the higher knock resistance.

Figures 230 to 236, which hardly require further explanation, give a survey of the other results of Townend.

Townend has also related the observed minimum ignition pressures to the critical compression ratios observed for the same materials. Even though a qualitative relation must exist, we regard the quantitative relations as of a more incidental nature, if only because of the role that the wall plays in Townend's experiments.

With the same phenomena of the cold flames are connected the

phenomena<sup>1</sup> observed in Jentzsch's ignition-point tester, except that here the introduction of the liquid phase and the undefined nature of the mixture composition brings in a new complication (in addition to

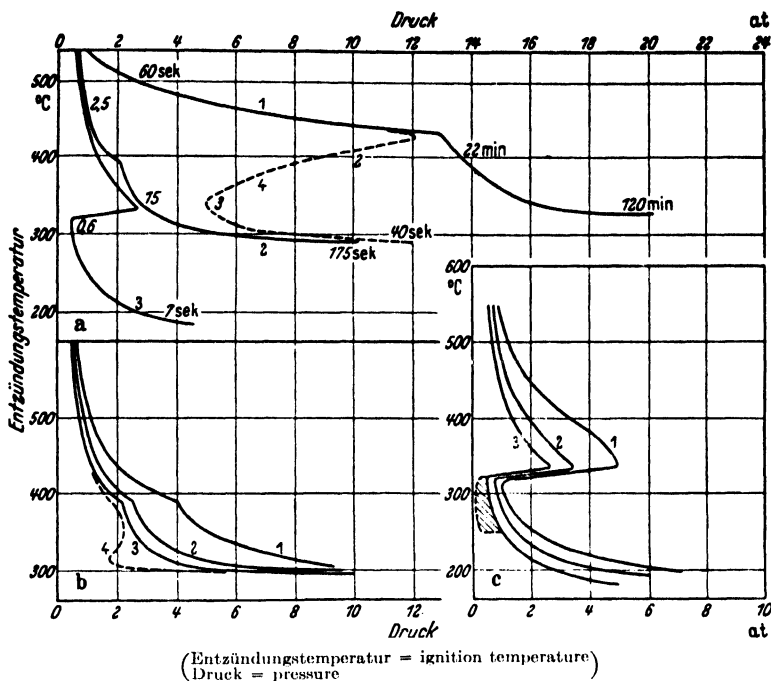


FIG. 231.—a is ignition of ethane-air mixtures with (1) 13 per cent ethane, (4) the same +1 per cent acetaldehyde, (2) and (3) mixtures corresponding to (1) of ethanol and acetaldehyde with air. Italicized numbers = induction periods in sec or min. b, (1), (2), and (3) represent curves for 4 per cent, 6.5 per cent, and 9 per cent, respectively, of ethanol in air. (4) corresponds to (1) but with +1 per cent acetaldehyde. c, (1), (2), and (3) represent 5 per cent, 7 per cent, and 10 per cent acetaldehyde in air. Shaded portion = range of cold flames. [From Townend et al., *J. Chem. Soc.* (1937).]

the influence of the wall). This does not of course exclude the fact that, with empirical calibration, the results obtained can be of practical use.

#### D. THE THEORY OF HYDROCARBON OXIDATION

As has been mentioned on page 418, Norrish<sup>2</sup> has thrown open to discussion a mechanism of methane oxidation that postulates the partici-

<sup>1</sup> Cf. JENTZSCH, H., *Z. Ver. deut. Ing.*, **68**, 1150 (1924). ZERBE, C., and F. ECKERT, *Öl. u. Kohle*, **2**, 112 (1934); *Z. angew. Chem.*, **45**, 593 (1932); **46**, 659 (1933). Cf. also DYKSTRA, F.J., and G. EDGAR, *Ind. Eng. Chem.*, **26**, 509 (1934). See also the comprehensive presentation on determining the auto-ignition temperatures by W. Helmore in "The Science of Petroleum," Vol. IV, p. 2970, Oxford, 1938.

<sup>2</sup> Cf. NORRISH, R.G.W., *Proc. Roy. Soc. London, A*, **150**, 36 (1935). NORRISH and J. WALLACE, *Proc. Roy. Soc. London, A*, **145**, 307 (1934). NORRISH and S.G. FOORD, *Proc. Roy. Soc. London, A*, **157**, 503 (1936).

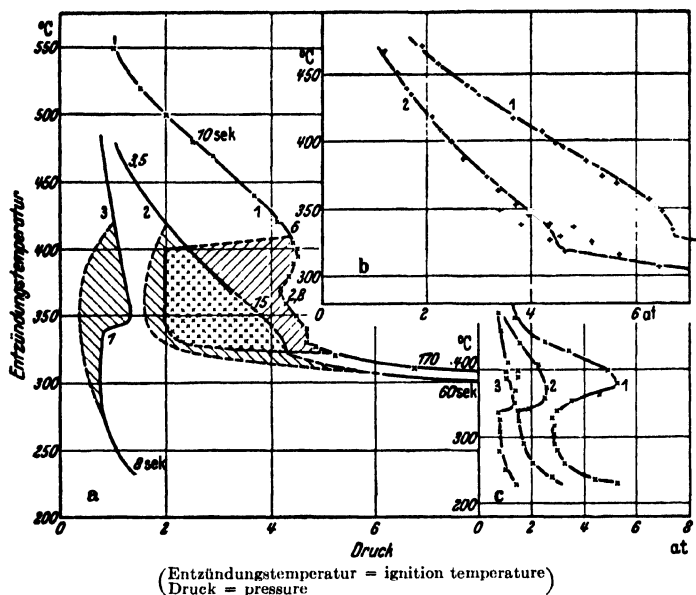


FIG. 232.—a, (1), (2), and (3) ignition of corresponding mixtures of propane, propanol, and propaldehyde (concentration figures lacking in the original). Shaded portion is the range of cold flames. Italicized numbers are induction periods in sec. b, (1) and (2) the same for 3 per cent and 7 per cent propanol in air. c, (1), (2), and (3) for 3 per cent, 5 per cent, and 10 per cent propaldehyde in air. [From Townend et al., *J. Chem. Soc.* (1937).]

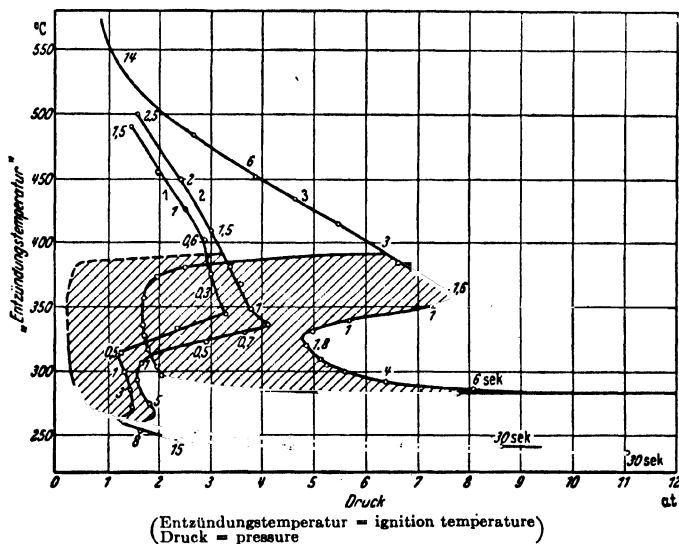


FIG. 233.—Ignition of corresponding mixtures of (1) *n*-octane, (2) *n*-heptane, and (3) iso-octane in air. Shaded portion is the range of cold flames. Italicized figures are ignition delays in sec. [From Townend et al., *J. Chem. Soc.* (1938).]

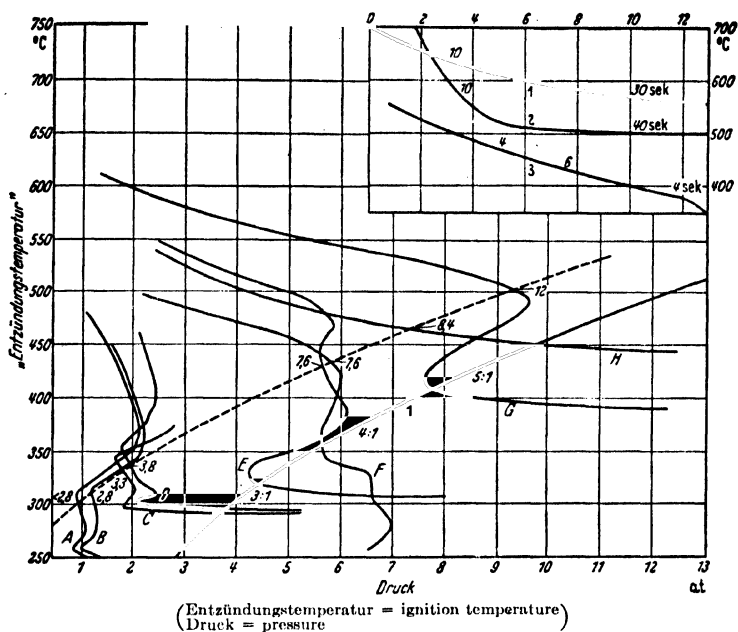


FIG. 234.—Curves for 1-sec ignition delay in theoretical mixtures with air of A, *n*-octane; B, *n*-heptane; C, *n*-hexane; D, *n*-pentane; E, iso-octane; F, di-isopropyl ether; G, propane; H, propylene. Solid curve 1 is pressure-temperature curve for adiabatic compression (compression ratio indicated). In order to estimate ratios under conditions of engine operation (induction periods  $\sim 5 \cdot 10^{-3}$  sec), the adiabat was arbitrarily moved to the left (dashed line); then follow the points of intersection with the individual fuels in the order of the critical compression ratios (shown). To the right above are curves for benzol 1, methane 2, and acetone 3. Italicized figures are induction periods in sec. [From Townend et al., *J. Chem. Soc.* (1938).]

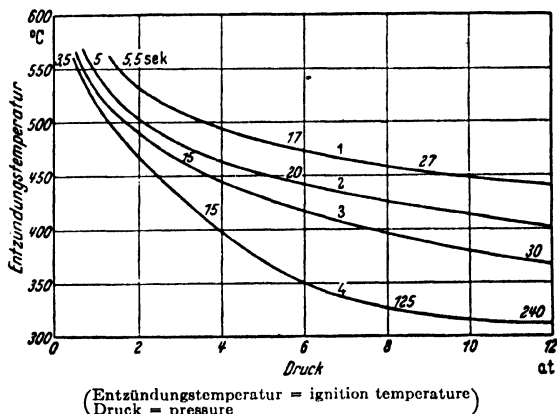


FIG. 235.—Ignition curves for ethylene-air mixtures with (1) 3 per cent, (2) 6 per cent, (3) 10 per cent, and (4) 20 per cent ethylene. Induction periods are in sec. [From Townend et al., *Proc. Roy. Soc., London, A*, vol. 160 (1937).]



pation of O-atoms and  $\text{CH}_2$ -radicals and that yielded remarkably good results in a formal respect. Sachsse (cited page 419) could use the same mechanism to account for the ignition of methane at high temperatures. It may therefore be assumed that essential portions of the formal relations derived by Norrish are correct. There are, however, certain objections to the special reaction stages assumed by Norrish, which are perhaps not absolutely convincing for methane but which for the higher

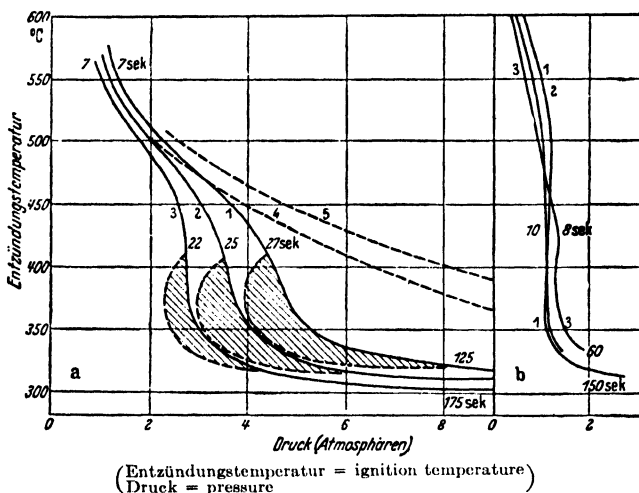


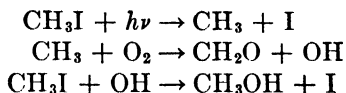
FIG. 236.—Propylene-air: *a*, with (1) 3 per cent, (2) 4.5 per cent, (3) 6 per cent, (4) 4.5 per cent propylene, for constant ignition delay of 3 sec; (5) the same for 2 sec. *b*, propylene-oxygen. (1) with 25 per cent, (2) 18 per cent, and (3) 10 per cent propylene. Italicized figures are induction periods in sec. Shaded portion is range of cold flames. [From Townend et al., *Proc. Roy. Soc., London, A*, vol. 160 (1937).]

hydrocarbons at any rate might lead to the rejection of a pattern proceeding chiefly by way of the oxygen atoms.<sup>1</sup> On the one hand, oxygen atoms are the most energy-rich of any of the radicals coming into consideration; their appearance therefore at low temperatures is relatively unlikely. On the other hand, the influence of artificially produced O-atoms on hydrocarbons from ethane and upward (cf. page 373) takes a course different from the usual hydrocarbon oxidation at low temperatures. In addition, the attack of O-atoms on hydrocarbons is connected with a luminescence that, in contrast to the luminescence observed in slow oxidation (formaldehyde bands), shows the normal flame spectrum. A

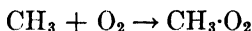
<sup>1</sup> For a discussion, cf. A.R. Ubbelohde, *Proc. Roy. Soc. London, A*, **152**, 354 (1935); *Z. Elektrochem.*, **42**, 468 (1936); further "The Science of Petroleum," Vol. IV, pp. 2937ff., Oxford, 1938. JOST, v. MÜFFLING, and ROHRMANN, *Z. Elektrochem.*, **42**, 488 (1936). LEWIS, B., and G. v. ELBE, *Ind. Eng. Chem.*, **29**, 551 (1937); *J. Am. Chem. Soc.*, **59**, 976 (1937); *Chem. Rev.*, **21**, 319 (1937); "Combustion, Flames and Explosions of Gases," Oxford, 1938.

participation of O-atoms in higher hydrocarbons seems, therefore, at least at low temperatures, to be excluded. The behavior of methane is, however, not so different from that of higher hydrocarbons that we should be compelled to postulate a specific mechanism for it. It therefore seems more satisfactory not to assume a participation of O-atoms at low temperatures.

Various photochemical oxidation reactions do not lead to a participation of O-atoms or  $\text{CH}_2$ -radicals, either.<sup>1</sup> Bates, for example, interprets his experiments on the photo-oxidation of methyl iodide by the reaction series<sup>2</sup>

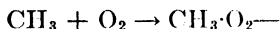


and believes he can add the reaction

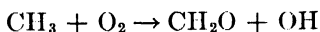


We should like to regard this conclusion as not absolutely convincing, especially since other observations have been made for ethyl iodide.

Schumacher and Brenschede investigated the photochemical oxidation of methane, methyl chloride, and methylene chloride, sensitized by chlorine. They were able to show that, in the photochemical oxidation of methane, sensitized by chlorine, a peroxidic intermediary product appears. For this reason, primary reactions of the radicals like



appear to us quite probable, even though in addition, especially perhaps at higher temperatures, Bates's reaction



is conceivable and probable. The assumption of the attachment of molecular oxygen to a radical fits in well with the elementary reactions usually adduced in oxidation reactions and especially well with what is known about aldehyde oxidation (*cf.* pages 378ff.).

Two fundamental difficulties stand in the way of a formal treatment of the kinetics of hydrocarbon oxidation: (1) the complicated role of the wall in conversion observed in most of the experiments and (2) the fact that a tremendously large number of elementary reactions are con-

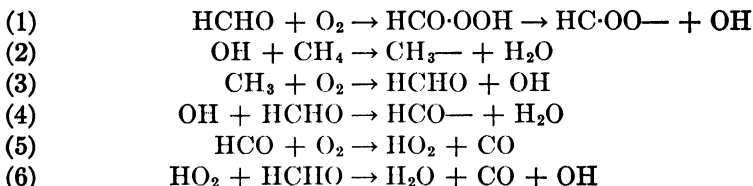
<sup>1</sup> Cf. SCHUMACHER, H.J., *Z. Elektrochem.*, **42**, 522 (1936). BRENSCHADE, W., and H.J. SCHUMACHER, *Z. physik. Chem.*, Sec. A, **177**, 245 (1937). BATES, J.R., and R. SPENCE, *J. Am. Chem. Soc.*, **53**, 1689 (1931). JONES, L.T., and J.R. BATES, *J. Am. Chem. Soc.*, **56**, 2285 (1934).

<sup>2</sup>  $h\nu$  means that a light quantum is being absorbed.

ceivable, among which we can experimentally arrive at a choice with difficulty or not at all. For that reason, every attempt at a detailed treatment of the combustion kinetics must be very speculative, and the more or less good agreement of the end formulas with experience does not as yet prove the correctness of the basic mechanism in detail. In spite of these uncertainties, such detailed computations are of value insofar as they indicate what formal conditions the reaction stages to be introduced must fulfill, what types of intermediary reactions are probable, and which are quite improbable.

Lewis and v. Elbe (cited page 432), to whom we refer for details, interpret methane oxidation, for example, by the following pattern:<sup>1</sup>

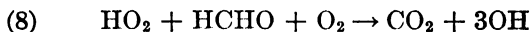
Chain induction at the wall:



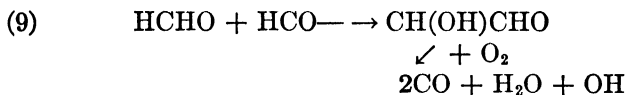
Chain-breaking at the wall:



Chain-branching:



Formaldehyde condensation:



Concerning this pattern, the following can be said: The assumption of HCO- and HO<sub>2</sub>-radicals (*cf.* also Chap. IX, page 317) is not improbable, nor is that of OH- and CH<sub>3</sub>-radicals at not too low temperatures. According to Groth,<sup>2</sup> the reaction (5) of HCO with O<sub>2</sub> is very probable. Chain-breaking, according to (7), might certainly take place if OH strikes the wall; except that, in addition to (7), a whole series of other breaking reactions come into consideration. The destruction of OH-radi-

<sup>1</sup> It is here assumed that traces of formaldehyde have been formed by a catalytic surface reaction.

<sup>2</sup> GROTH, W., and K. FALTINGS, *Z. Elektrochem.*, **44**, 621 (1938). Lewis and v. Elbe have recently called attention to the fact that partial reactions of the Lewis and v. Elbe pattern have been essentially supported by the observations of Groth and Faltings. (Lewis and v. Elbe, *Beitrag zur Tagung der Deutschen Akademie der Luftfahrtforschung, Schriften deut. Akad. Luftfahrtforsch.*, 1939.)

cals at the wall would, in particular, predominate only if OH were the least active radical and its concentration, therefore, considerably greater than that of other radicals. It is, however, probable that at least HO<sub>2</sub> is less reactionable than OH. The trimolecular branching reaction (8), which should proceed by way of an intermediary phase not listed, does not appear absolutely convincing; and, finally, the condensation of formaldehyde with the radical HCO would, according to similar examples, not appear to be improbable in solution. But since ion processes could be participating in solution, it is not clear from the outset whether a conversion of that kind is plausible for the gas phase. The oxidation of the condensation product in particular would require at least one more intermediary stage, since otherwise a quadrimolecular reverse reaction would be required for (9), which is completely excluded. Lewis and v. Elbe must assume that the velocity of (1) is given by

$$\frac{k_1}{d} [\text{HCHO}][\text{O}_2]$$

where  $d$  is the diameter of the container and where  $k_1$ , the velocity constant, like the others, bears the number of the reaction as an index.

With the further assumption<sup>1</sup> that  $\frac{2\lambda}{\epsilon d} \ll 1$ , they obtain, for the reaction velocity

$$-\frac{d[\text{CH}_4]}{dt} = \frac{k_1 k_2^2}{2\epsilon k k_4} \frac{[\text{CH}_4]^2 [\text{O}_2]}{k_7 - \frac{3k_2 k_5 k_8 [\text{CH}_4] [\text{O}_2]^2 [\text{M}] d^2}{k_4 k_6 \left\{ k_5 [\text{O}_2] + \frac{k_2 k_9}{2k_4} [\text{CH}_4] \right\}}}$$

In this,  $\frac{\pi^2 D^*}{r^2}$  ( $D$  the diffusion coefficient) equals  $\frac{k_7}{[\text{M}]d^2}$ , where  $[\text{M}]$  is the

total concentration of the gases present and  $\frac{2\lambda}{\epsilon r} = \epsilon k [\text{M}] d$ . Even though this velocity expression renders correctly a series of experimental facts on the dependence of the reaction velocity on the concentrations as well as on the diameter of the container, it will be possible, considering the many assumptions, to conclude from it only that we can represent the experimental facts with a similar radical chain mechanism.

It is a characteristic of the above reaction mechanism that it is probably necessary to demand of every mechanism that is in agreement with experience that a quasistatic concentration of formaldehyde

<sup>1</sup> Where  $\lambda$  = free path lengths,  $\epsilon$  = breaking probability at the wall,  $d$  = diameter of the container; in the computation, use is made of the formal relations derived in Lewis and v. Elbe, cited p. 274 (*cf.* Chap. VIII, pp. 273ff.).

\*  $r$  is the radius of the container.

appear (as well as of active intermediary products) and that the reaction velocity is proportional to the expression resulting from it. That is the reason why it is possible, in computing the initial increase in time of the formaldehyde concentration, to obtain also the induction period by means of this pattern. It is necessary to call to mind the fact that, according to Semenoff (*cf.* pages 281*ff.*), the assumption of long-lived intermediary products, like HCHO in this case, is necessary for the explanation of longer induction periods in chain reactions. The shortening of the induction period by the addition of aldehyde thus follows naturally and directly from this pattern. This would naturally follow from any pattern in which formaldehyde (or other substances) plays a similar role as intermediary product for the production of active centers.

The position of the explosion limits, too, and their susceptibility to not too small quantities of formaldehyde, turns out to be correct. To be sure, we must be cautious in our judgment in this case, since methane explosion is probably a CO explosion.<sup>1</sup>

Even though we are convinced that a number of details in the Lewis and v. Elbe pattern will have to be modified, it might nevertheless form a suitable point of departure for the further development of the theory of methane explosion.

The oxidation mechanism of the higher hydrocarbons has been repeatedly discussed.<sup>2</sup> At this point, it is necessary to explain the following: the appearance of the induction period, which in part, just as in the case of methane, might be interpreted by the building up of a certain aldehyde concentration,<sup>3</sup> perhaps in wall reactions; the appearance of the "cold flames" as well as of the "negative temperature coefficient" and of the reactions finally leading to ignition; and the nature of the reaction products—in addition to water, chiefly CO and aldehydes appear at low temperatures (as well as their oxidation and disintegration products), peroxides in small quantities, and CO<sub>2</sub> increasing with the temperature, olefins, alcohols, especially with a high ratio of hydrocarbon: oxygen as well as high pressures.

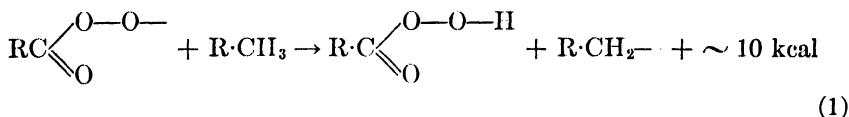
<sup>1</sup> That is, the transition into explosion takes place only after most of the methane is consumed and CO is the predominant reaction product (from a personal statement by W.E. Garner, *cf.* p. 417). Where an influence of formaldehyde is present, it is therefore probably more likely to assume that the conditions for thermal explosion have been reached by means of the general reaction acceleration; *cf.* Norrish, cited pp. 417–418.

<sup>2</sup> UBBELOHDE, A.R., cited pp. 382–488. JOST, v. MÜFFLING, and ROHRMANN, cited p. 465. LEWIS and v. ELBE, cited pp. 409, 425. NORRISH and FOORD, cited p. 417.

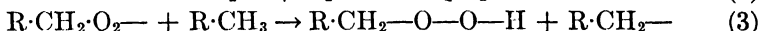
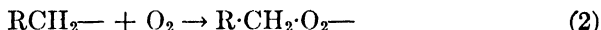
<sup>3</sup> But only under experimental conditions in which the wall exercises a considerable influence; not, for example, in ignition by adiabatic compression with a short induction period, as under the conditions of knocking combustion in the engine, and likewise not at higher temperatures.

Common to all the proposed mechanisms is the fact that they proceed by way of radical chains, as well as the assumption of peroxide-like radicals as intermediary products (with the exception of Norrish's pattern, which, for the reasons mentioned, we consider excluded in the higher hydrocarbons). Bone's hydroxylation pattern, by means of which it is possible to explain a great portion of the reaction products (but not the considerable repression of alcohol in favor of aldehydes) must be eliminated for theoretical reaction-kinetic reasons as well as for reasons dictated by direct experience.

Ubbelohde proceeds from Bodenstein-Bäckström's pattern of aldehyde oxidation and assumes the existence of an aldehyde radical  $\text{RC}=\text{O}$ , which has reacted with oxygen to form a peracid radical  $\text{RCO}(\text{OO})$  and which now reacts further with hydrocarbon according to



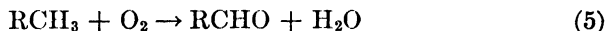
The alkyl radical produced reacts with oxygen to form a peroxide radical and the latter again with hydrocarbon



We should thus have a chain in which alternately peroxide radicals and alkyl radicals appear and by which alkyl hydroperoxide is formed. That peroxides are produced only in small quantities in hydrocarbon oxidation at low and at high temperatures (in contrast to aldehyde oxidation at low temperatures) is said to be conditioned by a well-known rearrangement and disintegration reactions of these peroxides,<sup>1</sup> for example,



where the gross conversion of hydrocarbon +  $\text{O}_2$  would then have to be represented by

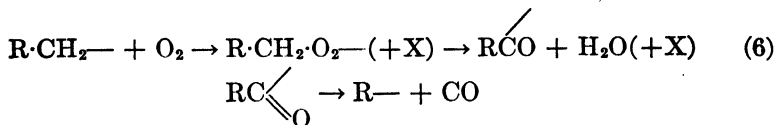


Thus the appearance of the aldehydes would have to be understood as a chief reaction product but not the disintegration into the next lower aldehyde with the simultaneous formation of CO to be assumed according to Pope, Dykstra, and Edgar.<sup>2</sup>

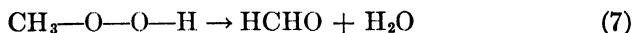
<sup>1</sup> Cf. RIECHE, A., cited p. 406.

<sup>2</sup> Cf. LEWIS and v. ELBE, cited pp. 432-456.

This result would, however, yield the following reaction, likewise suggested by Ubbelohde:<sup>1</sup>

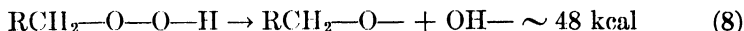


where the next lower radical would have to oxidize on to aldehyde. The transition peroxide aldehyde, for example,



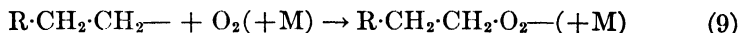
is known.

A chain-branching would be conceivable by the radical split of the peroxides

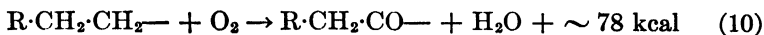


The fact of the negative temperature coefficient is obtained by assuming that, with rising temperature, the rest of the rearrangement and disintegration reactions of the peroxides increase more rapidly than this radical splitting.

Jost, v. Müffling, and Rohrmann (cited page 465) arrived at similar conclusions independently of Ubbelohde. First they started with the reactions of oxygen-hydrogen combustion (*cf.* pages 321*ff.*) and assumed that in part the same intermediary products could appear in hydrocarbon oxidation, and in part the reaction stages of the hydrocarbon radicals or molecules would be analogous to those of hydrogen atoms and molecules. This, analogous to  $\text{HO}_2$  formation, leads to reactions (if we also postulate<sup>2</sup> the existence of individual radicals like  $\text{R}\cdot\text{CH}_2\cdot\text{CH}_2-$ ) like



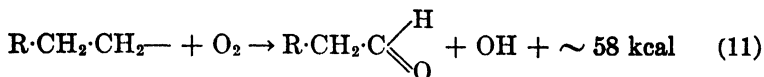
which can occur either in a triple collision (M is any molecule) or in multiatomic radicals, sometimes also in a double collision, and which correspond to Ubbelohde's reaction (2). As a resulting reaction (reaction of the peroxide radical), the formation of an aldehyde radical and of water would come into consideration [corresponding to (6)] or, also in one step,



and instead also

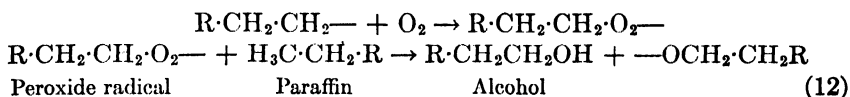
<sup>1</sup> X is any molecule that must be active as a collision partner.

<sup>2</sup> We are here in general formulating what has been proved originally in the case of  $\text{CH}_3\cdot$  and  $\text{C}_2\text{H}_5\cdot$ -radicals.

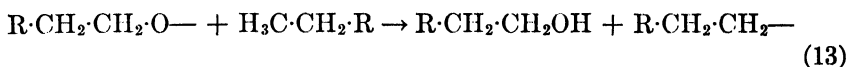


where (11) would again not lead to CO production, but rather the aldehyde radical appearing in (10) could, as Ubbelohde also assumed, split off CO, and the remainder could be further oxidized.<sup>1</sup>

That alcohol formation is favored by a high hydrocarbon concentration and high pressure would be conceivable by means of a reaction series like the following:

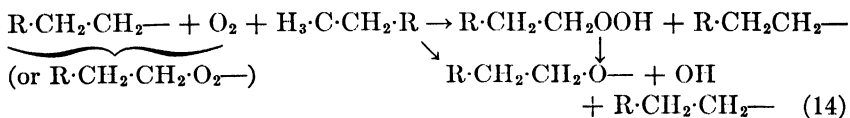


followed perhaps, by



or also the two steps of (12) combined in triple collision (12'). Both (12) and (12') mean that the alcohol was formed in a reaction of a higher order than aldehyde and would, as a result, describe the facts (*cf.* page 416).

The following was assumed as chain-branching:



This too is essentially equivalent to Ubbelohde's assumption, except that the alternative reaction without the intermediary formation of stable peroxide would indicate that the quantities of stable peroxides proved to be present in the reaction can be due to incidental conditions and need not be connected with the regular course of the reaction.

The branching reaction (14) is of the third order in contrast to the reactions (10) and (11), which are of the second order. This would indicate on the one hand that chain-branching and therefore the reaction velocity is considerably stimulated by a rise in pressure<sup>2</sup> and in the hydrocarbon concentration. If a triple-collision reaction (14) should make itself felt at all in addition to reactions of the type (10) and (11), the activation energy of the triple-collision reaction must be lower than that of the double-collision reactions. This, however, necessarily

<sup>1</sup> That the analogous radical HCO easily disintegrates, splitting off CO, is well known.

<sup>2</sup> A rise in the pressure will have a favorable effect on the reaction velocity for the additional reason that it reduces the diffusion of chain agents to the wall.



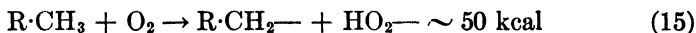
results in the following: If at low temperatures the triple-collision reaction with a low activation energy proceeds at a rate comparable with that of a double-collision reaction with a higher activation energy, the double-collision reaction will, at higher temperatures, dominate the triple-collision reaction. This means, however (in its final effect, in agreement with Ubbelohde; in its origins, varying in detail), that, with increasing temperature, chain-branching will again diminish, whereby the origin of the negative temperature coefficient becomes reasonable. The assumption of an intermediary product leading to chain-branching (in this case a radical), which, with rising temperature, is elsewhere more rapidly consumed instead of leading to branching, is therefore common to all the explanations advanced for this phenomenon. Under this heading would come also the assumption (Townend and associates, cited page 476) that aldehydes, which are present as intermediary products, disintegrate more rapidly with rising temperature than they are oxidized. Even though there are certainly experimental conditions under which these reactions are responsible for a negative temperature coefficient, the aldehyde disintegration takes place too slowly at low temperatures; and the fact that aldehydes appear in considerable concentrations among the reaction products of cold flames also contradicts this assumption as a generally valid explanation.

The formal nature of the intermediary reactions assumed by Ubbelohde as well as by Jost and his associates at any rate suffices to explain a number of the most important properties of hydrocarbon oxidation: the dependence on a higher power of the hydrocarbon concentration, the negative temperature coefficient, the favoring of the appearance of alcohols by high pressure and the raising of the ratio hydrocarbon:O<sub>2</sub>, the appearance of peroxides, as well as the ability of the peroxides to influence the reaction. Those assumed intermediary reactions definitely do not suffice, however, to account for the explanation of all the details of the reaction, and this was not intended at the time they were suggested; rather a general framework was sought that was to be supported later by more special assumptions founded on experiment.

Lewis and v. Elbe (cited pages 432, 456) attempted a discussion going beyond Ubbelohde and Jost. Besides what has been said above for methane (page 489), the following is to be added to this subject: The introduction of the radical HO<sub>2</sub>, which also plays a role in the oxygen-hydrogen reaction, has considerable probability in its favor. It is difficult to say whether the "peracid branching" resulting from the added effect of the HO<sub>2</sub> (*cf.* page 490) is probable in exactly the manner formulated by Lewis and v. Elbe. At any rate, the experimental findings of Lenher (page 406) and Egerton (page 434) support the fact that, under certain circumstances, H<sub>2</sub>O<sub>2</sub> is a primary product of peroxide

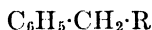
formation and that this might then probably have been produced by way of  $\text{HO}_2$ .

If  $\text{HO}_2$  formation plays an essential role, we could under certain circumstances think of the following primary reaction of hydrocarbon oxidation:

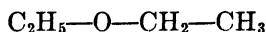


an endothermic reaction, but one that, in the case of the higher hydrocarbons, would be more favorable, from an energy point of view, than the corresponding reaction of  $\text{O}_2$  with  $\text{H}_2$  to form  $\text{HO}_2 + \text{H}$ . To be sure, Lewis and v. Elbe assume as the primary step an aldehyde-yielding reaction, probably catalytic. This might actually often be the case, especially under all conditions in which long induction periods appear, in which the wall can be proved to play a role, and in which small aldehyde additions greatly accelerate the reaction, or at least shorten the induction period. This does not apply in the case of a knock reaction in engines, however, and probably also not under the conditions in which Tizard and Pyc as well as Jost and Teichmann carried out their experiments on ignition by adiabatic compression. We are therefore forced to admit a second mechanism of chain induction. The above assumptions would do justice to the fact that this mechanism would have to predominate at higher pressures and temperatures. The catalytic reaction surely has a small temperature coefficient and would hence dominate the homogeneous bimolecular reaction (15) at low temperatures and pressures. At higher temperatures, the latter would then be determining. The same result would be achieved by assuming a primary disintegration of the radical of the hydrocarbon molecule, for which parallels can be found between the oxidation behavior and the thermal disintegration of hydrocarbons,<sup>1</sup> although difficulties might arise because of the required chain length as well as the absolute value of the activation energy.

It is not entirely easy to explain the point of the primary attack on the hydrocarbon molecule. According to Pope, Dykstra, and Edgar, it would have to be the end C-atom in paraffins; in aromatics, it is (*cf.* page 469; also A.R. Ubbelohde, page 488) the  $\alpha$ -C-atom

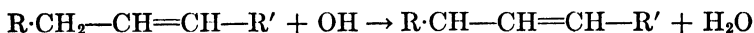


which is reasonable in view of the double-bond rule; in the case of ethers, it is the group bordering on oxygen

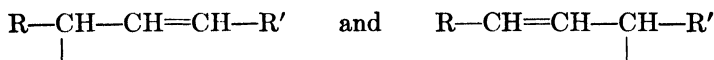


<sup>1</sup> BOERLAGE, G.D., and W.J.D. VAN DYCK, *J. Inst. Petroleum Tech.*, **21**, 40 (1935). JOST, v. MÜFFLING, and ROHRMANN, cited p. 465.

Whether in the case of the higher olefins—corresponding to the double-bond rule—the attack takes place at a different point than in the paraffins cannot as yet be said with any certainty, but experience speaks against it, since a characteristic difference between paraffin and olefin oxidation cannot be established. The double-bond rule does indicate, however, that higher olefins convert with free radicals, forming especially long-lived, stable radicals and have a chain-breaking effect; that, in other words, higher olefins are more stable in oxidation than the corresponding paraffins. We could, for instance, imagine a reaction like

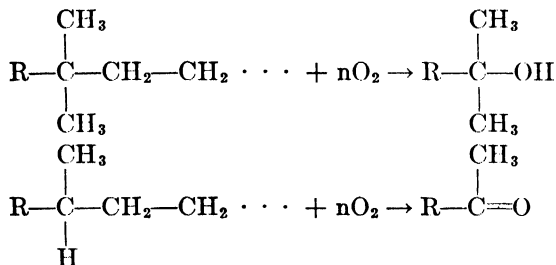


in which the radical produced would, because of the resonance between the two structures



(or, written as an intermediary condition,  $R-\underset{\textstyle |}{\underset{\textstyle |}{CH}}\cdots\underset{\textstyle |}{\underset{\textstyle |}{CH}}\cdots\underset{\textstyle |}{\underset{\textstyle |}{CH}}-R'$ ) be

especially stable and sluggish in reaction. That branched paraffins are more stable than extended paraffins could be explained by the fact that a continued destruction of the molecule by way of aldehydes and aldehyde radicals would not be possible here but rather that, in place of branching, finally either a tertiary alcohol or a ketone would have to be formed



The greater oxidation stability and knock resistance of these materials as opposed to the aldehydes, however, is known (pages 454*ff.* and 559).

To be sure, attention should be called to the fact that it has thus far not been possible to prove the corresponding higher ketones in the disintegration of the higher branched paraffins.<sup>1</sup> Nevertheless acetone appears in larger amounts in the oxidation of 2,5-dimethyl hexane.

<sup>1</sup> BEATTY, H.A., *Chem. Rev.*, **21**, 328 (1937).

There is no fundamental difficulty in understanding the inhibition of hydrocarbon oxidation by means of antiknocks, since it is a matter of a chain reaction. In the effect of lead or iron, it can be a matter either of the reduction of an oxygen-containing intermediary product, probably a radical, by means of the metal or a low oxide, or of the oxidation of an intermediary product by means of metal oxide. The corresponding experiments are not definitive. If Egerton and Gates (cited page 443) found that  $\text{Pb}(\text{C}_2\text{H}_5)_4$  must have disintegrated in the presence of  $\text{O}_2$  in order to be effective, then this merely indicates that undisintegrated lead tetraethyl does not inhibit the reaction. That, likewise according to Egerton and associates (page 548), metals introduced into the engine in the presence of oxygen have a stronger antiknock effect than when introduced in the presence of nitrogen does not necessarily mean that they are effective only in the oxide stage; for in the engine there is always occasion for oxidation as well as reduction. It might in this case simply be a matter of an influence on the distribution condition that the oxygen perhaps prevents the metal particles from coagulating to larger particles. Thus it could also be understood that Berl,<sup>1</sup> in apparent contradiction to Egerton, found that colloidal lead mixed with the gasoline had an antiknock effect that was lacking when colloidal lead oxide was added. We should have to assume only that lead oxide was of a coarser dispersion than the metallic lead.

In general, we are of the opinion that the course of hydrocarbon oxidation is represented by and large by the following assumptions: radical chain mechanism with branching (branching in the gas phase and probably with the added effect of the wall); chain induction and breaking can take place, depending on the experimental conditions, at the wall and/or in the gas phase; in case of chain induction at the wall, probably added effect of the aldehydes; peroxidic radicals take part in the reaction, probably peracid radicals, also  $\text{HO}_2$ . The formation of  $\text{CO}$ ,  $\text{H}_2\text{O}$ , aldehydes, and peroxides is easily accounted for by this pattern;  $\text{CO}_2$  could, among other things, be produced in the disintegration of acids or peracids originating from aldehydes. For the formation of lower hydrocarbons as well as of olefins, the intermediately produced alkyl radicals could be responsible. Chain induction in the gas phase, to be assumed at higher pressure and temperatures, could proceed from a primary radical disintegration of the hydrocarbon or a reaction of oxygen with the hydrocarbon, which is not yet entirely clear in detail [reaction (15), page 497]. Any attempt at a detailed treatment of the kinetics

<sup>1</sup> BERL, E., K. HEISE, and K. WINNACKER, *Z. physik. Chem.*, Sec. A, **139**, 453 (1928). BERL, E., and K. WINNACKER, *Z. physik. Chem.*, Sec. A, **145**, 161 (1929); **148**, 36, 261 (1930). Cf. also LORENTZEN, J., *Z. angew. Chem.*, **44**, 130 (1931). TAUSS, J., H. GORLACHER, and J. LORENTZEN, *Z. angew. Chem.*, **44**, 693 (1931).

must for the time being be highly speculative, for which reason we shall omit it here. We refer to the discussion in Lewis and v. Elbe, emphasizing that the taking over of well-known condensation, disintegration, and rearrangement reactions of organic compounds, especially of a peroxidic nature (Rieche, page 406), is meaningful only if we are convinced that it is not a matter of reactions that are specific for the condensed condition.<sup>1</sup>

<sup>1</sup> Cf. in this connection also the papers at the meeting of the Deutsche Akademie der Luftfahrtforschung, Berlin, 1939, to appear in the publications of the academy.

## CHAPTER XII

### COMBUSTION IN OTTO ENGINES

#### 1. Survey of the Observed Phenomena and Their Interpretation.—

Internal-combustion engines probably represent the most important field in which a mastery of the processes of combustion is essential. We are here limiting ourselves to machines of the type of the Otto engine, since special conditions that will be taken up in the next chapter appear in Diesel engines with heterogeneous mixture of fuel and air.

Thermodynamic treatment of the ideal process, which is taken into consideration for reasons of comparison, shows<sup>1</sup> that the efficiency of the Otto engine is favorably influenced by an increase in compression. It is furthermore immediately clear that the absolute performance increases with the load and therefore with overload. The increase in compression, however, as well as overloading, is limited by the appearance of knocking. This term designates a process of combustion accompanied by a metallic, knocking noise. The following description does justice to the external process of knocking combustion: A certain remaining fraction of the charge in the motor burns instantaneously (or with a speed extraordinarily increased in comparison with the normal flame speed) so that the volume of this remaining part does not change noticeably during combustion. As a consequence, essentially higher temperatures and, under certain circumstances, pressures several times higher than are normally reached occur in combustion in this part. From this variation of pressure, a percussion wave develops that shows as oscillations in the indicator diagram. Parallel with this go an excessive mechanical and heat demand on the engine, an increased thermal transition, and a decline in output.<sup>2</sup>

The origin of knocking is as follows:<sup>3</sup> The compressed mixture in the engine reaches a temperature that is quite high before ignition (*cf.* page 510). This temperature further increases in the last part of the unburned charge as a consequence of compression by the progressing flame. These temperatures are so high that almost all fuels that are

<sup>1</sup> For readers less familiar with engines, these matters have been put down in the following section, pp. 503ff.

<sup>2</sup> *Cf.* SCHMIDT, E., Vortrag auf der Tagung der deutschen Akademie der Luftfahrtforschung, 1939.

<sup>3</sup> These explanations are documented theoretically and experimentally in Sec. 3, pp. 510ff.

actually in use are subject to a rapid oxidation. It depends on the length of time that elapses between the development of an explosion from this rapid reaction whether the remnant of the charge reacts more or less instantaneously before the flame has progressed through the entire combustion chamber and whether knocking will occur or not.<sup>1</sup> Since the speed of chemical reaction in general rises sharply with a rise in temperature, any rise in temperature is bound to increase knocking. Increase in compression, increase in temperature of the air and of the cooling agent, and overloading have this effect. In the latter case, dissociation of the combustion gases because of the pressure decreases, and temperature (indirectly also that of the unburned gases) increases. Furthermore, relative heat loss decreases with increasing pressure. Tizard<sup>2</sup> pointed out long ago that the suspected influence of pressure on knocking might in reality be primarily a matter of temperature.

All experiences with the oxidation of hydrocarbons have shown that we are dealing with chain reactions (*cf.* the preceding chapter) that may be greatly retarded or accelerated by the addition of small quantities of various substances. Even if we do not yet understand in detail the mechanism of these changes, it is quite right to interpret the influence of proknock substances like peroxide and nitrites, as well as the influence of antiknock substances like aniline, iron carbonyl, and lead tetraethyl<sup>3</sup> as an interference in the process of chain reactions. Beyond this, we can also explain in this manner the ways in which various fuels can be influenced by the addition of knock compounds, as well as their behavior in mixtures.<sup>4</sup>

As a matter of principle, it would be possible to make preliminary calculations concerning the knock behavior of individual fuels as soon as the mechanism of oxidation is explored; but at present such calculations are prevented by our lack of information about the distribution of temperatures<sup>5</sup> in time and space in the gas mixture inside the engine. In addition, we have the problem that knocking, in turn, influences the temperature condition of the engine, for which reason a power decrease in an engine operating on knock-producing fuel occurs only after a certain period of operation.<sup>6</sup> For these reasons, a purely theoretical

<sup>1</sup> These explanations can be proved in detail; *cf.* pp. 510ff. Thus the flame speed indirectly plays a role in knocking.

<sup>2</sup> TIZARD, H.T., *Trans. Faraday Soc.*, **22**, 352 (1926).

<sup>3</sup> Discovered as an antiknock substance by T. Midgley, Jr., *SAE J.*, **7**, 489 (1920); *cf. Ind. Eng. Chem.*, **14**, 589, 849, 894 (1922).

<sup>4</sup> *Cf.* Sec. 9, pp. 553ff.

<sup>5</sup> The averages of time and space for these, which are relatively easy to obtain, cannot be used for this purpose.

<sup>6</sup> *Cf.* the comprehensive treatment by von Philippovich, *Z. Elektrochem.*, **42**, 472 (1936).

treatment of knocking in the practical operation of engines is for the present out of the question; but even without this, the theoretical findings allow some practical interpretations.

**2. General Fundamentals and the Thermodynamics of Combustion in Engines.**—The method of operation of the Otto engine may be assumed as known: In the four-stroke engine, the first stroke draws in the mixture of fuel and air. During the second stroke, this is compressed, ignited at the end of compression, and, ideally, instantaneously burned. In the third stroke, the burned gases expand and perform work. During the fourth stroke, the exhausting of the burned gases takes place. Thus one cycle requires two revolutions of the crankshaft.<sup>1</sup> Since the work required during the suction stroke and the exhaust stroke, aside from other friction losses, is caused by the fact that the mixture must be transported with finite speed through conduits with finite friction resistance, which is not essential to the process, we are justified in assuming the following ideal process<sup>2</sup> (Fig. 237) in order to compare the performance that has been reached with that which might be reached under the optimum conditions.

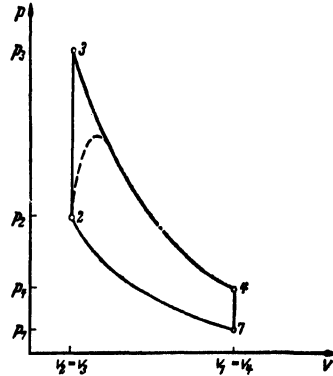


FIG. 237.—Ideal process of the Otto method.

An ideal gas (air) is assumed as the working substance in the cylinder with an initial volume of  $v_1$  and initial pressure  $p_1$  (and initial temperature  $T_1$ ). Let adiabatic compression take place to  $v_2, p_2, T_2$ . Now let the heat quantity  $Q_1$  be instantaneously supplied (corresponding to infinitely fast combustion), so that under constant volume the pressure rises to  $p_3$  and the temperature to  $T_3$ . This is represented by

$$(T_3 - T_2)\bar{c}_1 = Q_1 \quad (1)$$

$\bar{c}_1$  representing the mean heat capacity of the gas mixture between  $T_2$  and  $T_3$ . From 3 to 4, the gas expands adiabatically with work output to  $v_4 = v_1$ , at  $p_4$  and  $T_4$ . Now let the heat quantity  $Q_2$  be rejected

$$(T_4 - T_1)\bar{c}_2 = Q_2 \quad (2)$$

where  $\bar{c}_2$  is the mean heat capacity between  $T_4$  and  $T_1$ , so that the initial condition is reached again.

<sup>1</sup> The two-stroke process, in which these occurrences are combined in one revolution of the crankshaft, offers nothing new in matters of interest to us and is therefore left out of consideration.

<sup>2</sup> Cf. MÜLLER-FOUILLET, "Lehrbuch der Physik," Vol. III, 1, and the chapter on technical thermodynamics; also PYE, D.R., "Combustion Engines."



The work done, represented by the area 1,2,3,4 (Fig. 237), is

$$A = Q_1 - Q_2 \quad (3)$$

The efficiency, in reference to the heat supplied  $Q_1$

$$\eta = \frac{A}{Q_1} = 1 - \frac{Q_2}{Q_1} \quad (4)$$

If  $\epsilon_1 = \epsilon_2$ , it follows further<sup>1</sup> that

$$\eta = 1 - \frac{T_4 - T_1}{T_3 - T_2} = 1 - \frac{T_1}{T_2} \frac{\frac{T_4}{T_1} - 1}{\frac{T_3}{T_2} - 1} \quad (5)$$

If we consider that 1 and 2 as well as 3 and 4 are connected by an adiabatic curve, so that

$$p_1 v_1^\kappa = p_2 v_2^\kappa \quad (6a)$$

$$p_3 v_3^\kappa = p_4 v_4^\kappa \quad (6b)$$

there follows, because  $v_2 = v_3$  and  $v_1 = v_4$ ,

$$\frac{p_1}{p_2} = \frac{p_4}{p_3} \quad (7)$$

and because of the gas laws also

$$\frac{T_1}{T_2} = \frac{T_4}{T_3} \quad (8)$$

so that

$$\eta = 1 - \frac{T_1}{T_2} = 1 - \left( \frac{v_2}{v_1} \right)^{\kappa-1} \quad (9)$$

If we introduce as the compression ratio

$$\epsilon = \frac{v_1}{v_2} \quad (10)$$

the well-known formula for efficiency results

$$\eta = 1 - \frac{1}{\epsilon^{\kappa-1}} = 1 - \epsilon^{1-\kappa} \quad (11)$$

From this, it is clear that the efficiency of an engine becomes greater in proportion to increased compression ratios (Table 103, Fig. 238). In

TABLE 103.—THERMAL EFFICIENCY  $\eta$  OF AN OTTO ENGINE AS A FUNCTION OF THE COMPRESSION RATIO  $\epsilon$  FOR THE AIR PROCESS AND  $\kappa = 1.4$  (FROM PYE<sup>1</sup>)

|              |      |      |      |      |      |      |      |      |      |      |      |      |      |
|--------------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| $\epsilon =$ | 2    | 3    | 4    | 5    | 6    | 7    | 8    | 10   | 12   | 14   | 16   | 18   | 20   |
| $\eta =$     | 0.24 | 0.35 | 0.42 | 0.47 | 0.51 | 0.54 | 0.56 | 0.60 | 0.63 | 0.65 | 0.67 | 0.68 | 0.69 |

<sup>1</sup> PYE, D.R., quoted p. 503.

<sup>1</sup> This is never the case, because of the temperature variation of the specific heats.

actual practice,  $\kappa$  is not 1.4, for the specific heat of the air rises with the temperature, and  $\kappa = \frac{c_p}{c_v} = \frac{c_p}{c_p - R}$  accordingly decreases with rising temperature. Furthermore, the specific heat of the fuel is higher than that of air, and also higher than that of the products of combustion. All

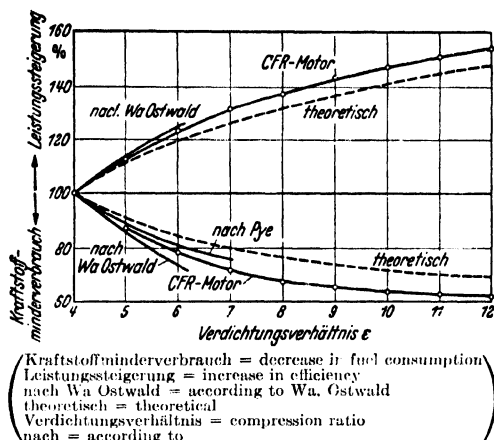


FIG. 238.—Increase in efficiency and decrease in fuel consumption with increase of compression ratio, theoretical as well as according to special experiments. (From Giessmann.<sup>1</sup>)

this has the effect of decreasing the efficiency. In reality, we shall have to expect  $\kappa$  values of  $\sim 1.3$  to  $\sim 1.35$  or lower. Table 104 shows what effect this has with regard to ideal efficiency. If  $\kappa$  is reduced from 1.4 to 1.3, the theoretical efficiency decreases by about 20 per cent. Figure 238 represents, according to Giessmann's graphs,<sup>1</sup> the relative increase

TABLE 104.—THERMAL EFFICIENCY  $\eta$  AS A FUNCTION OF  $\epsilon$  FOR  $\kappa = 1.4$  AND  $1.3^*$

| $\epsilon =$                  | 4    | 6    | 8    | 10   |
|-------------------------------|------|------|------|------|
| For $\kappa = 1.4$ , $\eta =$ | 0.42 | 0.52 | 0.56 | 0.61 |
| For $\kappa = 1.3$ , $\eta =$ | 0.34 | 0.41 | 0.46 | 0.50 |

\* Calculated final pressure; see Table 105, p. 510.

in output with corresponding decrease in fuel consumption. It is not surprising to find the practical relative increase in output (or decrease in fuel consumption) more favorable than they should be according to the theoretical curve, because the increase in efficiency with increasing compression is not the only practical effective influence. There is also, for example, among other things the decrease in heat loss. On the whole, this simply means that practical efficiency is relatively lower than the theoretical data with low compression than with high compression.

<sup>1</sup> GIESZMANN, W., *Z. Ver. deut. Ing.*, **80**, 833 (1936).

A question we shall not deal with is the fact that sharply rising peak pressures impose constructional limits at the highest compression ratios. On the other hand, we shall have to deal in detail with the limitations that the characteristics of combustion of the fuel impose on the increase in compression.

First, however, we shall deal with other influences that combustion exerts on the efficiency of the engine. In Fig. 237, we can see that ideal efficiency presupposes an instantaneous heat supply at 2; i.e., in actual engines, if ignition takes place at 2, an infinitely high speed of combustion is assumed. If combustion takes place with finite speed, the area of the  $p-v$  diagram decreases, and with it the efficiency (dotted line in Fig. 237). This would take place not only because of finite combustion speed, but also because of the finite delay in ignition. If the spark occurs at 2 (cf. Chaps. III, IV), the effect of ignition delay and of finite flame speed is to a great extent compensated for by advancing the time of ignition; i.e., the spark is formed before upper dead center, the necessary adjustment depending on the rotative speed. If we had a normal combustion speed of the order of  $< 1$  m/sec (cf. Chap. III, page 123), the time of combustion in cylinders of the order of magnitude 1 dm would take about 0.1 sec. Since at 3000 rpm there would be available only 0.01 sec per piston stroke, the operation of a fast-running combustion engine would be economically impossible. Fortunately, however, the conditions under which the flame propagation takes place by means of normal burning speed alone, excluding currents, are never present in the engine. Even without special provisions, there are always gas movements from suction and compression present in the engine that bring about an increase in the actual combustion velocity. By means of favorable shaping, arrangement of valves, etc., the turbulence of the gases in the cylinder head can be even further increased artificially.<sup>1</sup> Measurements of flame speeds in engines actually always yield higher values—from about 10 to 30 m/sec for the flame speed—and no difficulties are experienced in engines from that source.

Schnauffer,<sup>2</sup> by the method of ionization,<sup>3</sup> determined flame speeds in airplane engine cylinders, which he determined as 12 to 23 m/sec at 1900 rpm, compared with about 2 to 6 m/sec in bombs under otherwise equal conditions. The average combustion speed is approximately proportional to the whirling speed.

<sup>1</sup> Cf. RICARDO, H.R., cited p. 507.

<sup>2</sup> SCHNAUFFER, K., *Z. Ver. deut. Ing.*, **75**, 455 (1931). Cf. further *Ver. deut. Ing. Forsch.*, 1931, as well as *Jahrb. deut. Versuchsanst. Luftf.*, 1931, p. 375; 1930, p. 304.

<sup>3</sup> At known distances, there are metal probes, introduced as insulated pairs, between each of which exists an electrical potential; a flow of current takes place in consequence of ionization when the flame front progresses. The occurrence of this is chronologically registered.

According to Eq. (11), the ideal efficiency of the engine would be independent of all special influences insofar as they leave the values of  $\epsilon$  and  $\kappa$  unaffected. Aside from the influence on  $\kappa$  (*cf.* page 515), an increase of cycle process temperature also has an unfavorable effect, because the position of the dissociation equilibriums of the combustion occurring in combustion is changed, which results in a less complete conversion and a lower efficiency.<sup>1</sup> On the whole then, we are interested in working for temperatures as low as possible, coupled with large  $\kappa$  values and small degrees of dissociation.

As an illustration, we give the cycle (progress) temperatures and pressures calculated by Ricardo<sup>2</sup> for a special case. The suction mixture has a pressure of 0.989 atm abs and a temperature of 398° abs in consequence of preheating by the cylinder walls and mingling with the hot exhaust products. With a compression ratio 5:1, the mixture reaches a compression pressure of 8.65 atm abs with a temperature of 698° abs. At the end of combustion,  $T = 2753^\circ$  abs and  $p = 35.75$  atm abs; at the end of expansion,  $T = 1948^\circ$  and  $p = 5.05$  atm abs. With higher compression conditions, pressures and temperatures become correspondingly higher; the temperature at the end of expansion, however, becomes lower. The heat of vaporization of the fuel plays a perceptible role in the suction temperature of the mixture in the cylinder. In the case of fuels with especially high heat of vaporization, *e.g.*, alcohol,<sup>3</sup> this has the effect of a perceptible lowering of the temperature of the mixture. Ricardo, for instance, gives the following value for lowering of mixture temperature because of evaporation of the fuel. We reproduce only a few typical examples:

| Substance   | <i>n</i> -Hep-<br>tane | Benzol | Cyclo-<br>hexane | Heptylene | Ethanol | Methanol |
|---|------------------------|--------|------------------|-----------|---------|----------|
| Lowering of mixture<br>temperatures owing<br>to evaporation . . . . . | 18°                    | 26°    | 21.5°            | 23°       | 82.7°   | 140°     |

This lowering of mixture temperature favorably affects the efficiency (the quantity of the suction mixture increases), especially the knock reaction, which depends considerably on temperature (*cf.* also pages 533*ff.*).

Since the initial temperature in general cannot be lowered, the only consideration in lowering the cycle process temperature—within the ideal picture (Fig. 237)—is a decrease of the heat supplied,  $Q_1$ . (To be sure, efficiency is independent of the *amount*, whereas of course the actual output per working stroke does depend upon the amount.) It

<sup>1</sup> *Cf.* KÜHL, H., *Ver. deut. Ing. Forsch.*, **373** (1935).

<sup>2</sup> RICARDO, H.R., "Schnellaufende Verbrennungsmotoren" (High-speed Internal Combustion Engines) Berlin, 1932.

<sup>3</sup> The important thing here is not the heat of vaporization per mol, but rather the heat of vaporization of the quantity necessary for the reaction with the suction air, *i.e.*, many more mols for alcohol than for benzol, which has a similar boiling point, or for corresponding paraffins.

means that in practice a diminution of the fuel content of the suction air, i.e., the use of lean mixtures, has a favorable effect on efficiency. Even with constant temperature,  $\kappa$  changes with the composition.

Figure 239 shows, according to Ricardo, the connection between thermal efficiency and mixture composition as well as the average effective piston pressure (to which absolute output is proportional). Actually, thermal efficiency (curve *b*) increases at first quite sharply in the direction of excess air with low combustion temperature; but poor ignitibility and the low combustion velocity of the lean mixtures prevent further increase, and efficiency again drops. With the absolute output, the situation is reversed; it reaches its maximum with excess fuel. In the

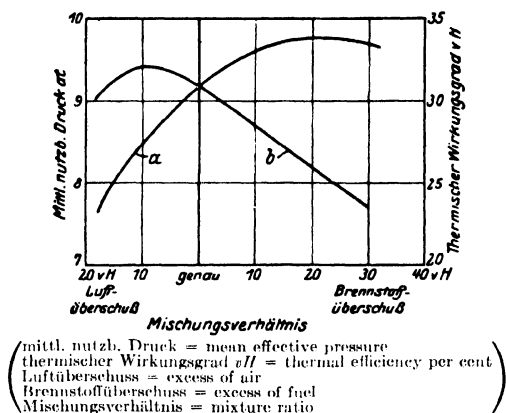


FIG. 239.—Variation of the mean effective piston pressure *a*, as well as of the thermal efficiency *b* with mixture composition. (From Ricardo, p. 497.)

case of illuminating gas, where the limits of inflammability lie farther apart than for benzene, thermal efficiency increases up to  $\sim 40$  per cent excess air and beyond.

With use of lean mixtures, on the one hand, we approach the lower limit of ignition (*cf.* Chap. III), which in the case of irregular distribution to the different cylinders of a multicylinder engine may easily be exceeded; on the other hand, flame speed becomes very low. These two considerations limit the favorable efficiency otherwise attainable with lean mixtures. Thus the unsolved problem still exists: to influence combustion in such a way that it proceeds sufficiently rapidly even in lean mixtures and to cause certain ignition. Since we cannot, generally speaking, appreciably influence combustion by the addition of small quantities of chemicals—exceptions like the modification of the burning speed of CO by  $H_2$  or hydrogen-containing substances cannot be adduced as proof in the behavior of hydrocarbons—there exists little hope of finding a simple means of improvement. It might be possible, however, if we

produce fuel synthetically anyhow or give supplementary treatment to natural products, to work for combinations that have the lower ignition limit as low as possible and at the same time have a combustion velocity as high as possible. In any case, it should be pointed out that questions of flame speed (to which ignition limits are closely related) are also

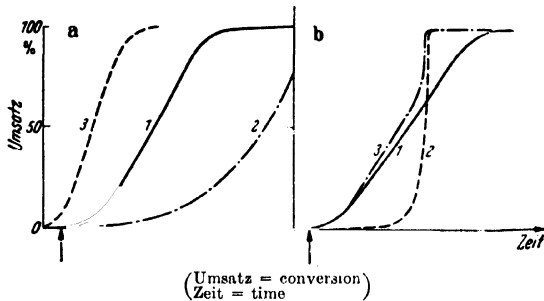


FIG. 240.—Time conversion curve for combustion in the engine. *a* 1, curve for normal combustion; 2, curve for spontaneous reaction in the unburned mixture; 3, the same for advanced ignition. *b* 1 corresponds to *a* 1; 2, curve for spontaneous reaction in unburned mixture with knocking; 3, resulting conversion curve from 1 and 2, with knocking. ↑ = moment of ignition.

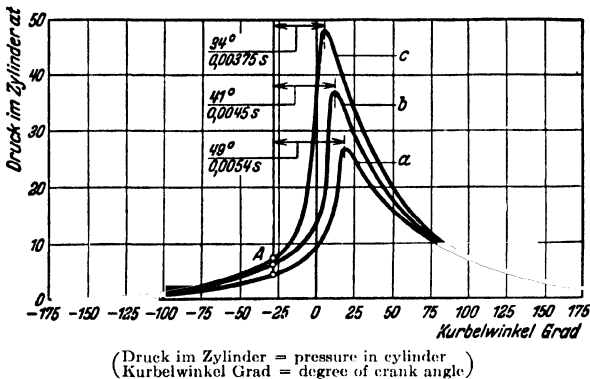


FIG. 241.—Influence of the compression ratio on combustion velocity. *a*, compression ratio 4:1, mean effective piston pressure 8.4 atm. *b*, compression ratio 5:1, mean effective piston pressure 9.6 atm. *c*, compression ratio 6:1, mean effective piston pressure 10.3 atm. Pre-ignition constant 30° at *A*, speed 1500 rpm. Exact gasoline-air mixture.

important in engine operation (*cf.* Chap. III). Flame speed also has its effect on knocking (*cf.* page 524).

**3. The Knocking Process.**—The most important hindrance to an improvement of the efficiency through increasing compression, or—for that matter—of increasing output through overloading, lies in the process of combustion with the occurrence of knocking.

If the conversion in the engine caused by normal progression of combustion is recorded as a function of time, the qualitative picture of

Fig. 240 results. Conversion and pressure show a similar rise (by measurement of pressure, conclusions can be drawn concerning conversion). The speed of pressure increase also depends on various external factors like size and shape of the combustion chamber, position of the spark plug, and whirl of the mass of gas (*cf.* Ricardo, cited page 507).

As an example of the actual pressure variation in the engine, we reproduce in Fig. 241 an indicator diagram (Pye, cited page 503).

As already mentioned, efficiency would decrease with too slow a rise in pressure; but it seems it has always been practically possible to counteract this. Too quick a rise (*i.e.*, according to engine and operating conditions, more than about 2 to 3 atm/deg of crank angle; after Ricardo, cited page 507) leads to a rough running of the engine, which must be avoided. This too can be overcome by features of design.

The more serious difficulties that come up have a different reason. The gases drawn into the engine are under considerable pressure and temperature at the end of compression. If we assume 80°C as the initial temperature,<sup>1</sup> the following compression pressures  $p_2$  and temperatures  $T_2$  result with  $\kappa = 1.35$  and different compression conditions (Table 105).

TABLE 105  
 $\kappa = 1.35$        $T_1 = 353^\circ \text{ abs}$        $p_1 = 1 \text{ atm abs}$

| $\epsilon$ .....     | 4   | 5   | 6    | 7    | 8    | 9    | 10   |
|----------------------|-----|-----|------|------|------|------|------|
| $T_2$ , °C.....      | 300 | 347 | 387  | 425  | 457  | 490  | 518  |
| $p_2$ , atm abs..... | 6.5 | 8.8 | 10.5 | 13.0 | 16.6 | 19.5 | 22.4 |

This table shows that, even with low compression, final temperatures and pressures are reached under which a lively reaction can take place in the mixture of hydrocarbon and air (*cf.* Chap. XI), which, in the case of many hydrocarbons, must lead to auto-ignition after rather short periods of induction.

The temperatures given above are not, however, the maximum temperatures that a mixture attains inside the engine. Let us take a practical example: With a compression ratio of  $\epsilon = 7$ , for instance, a maximum pressure of about 40 atm was reached. The final part of the mixture has been compressed up to this pressure by the other, burning part. Without heat loss, we should calculate with  $\kappa = 1.35$  a temperature of  $\sim 6409^\circ\text{C}$ . Actual heat losses tend toward decreasing the temperature; but, since the initial temperature of  $80^\circ\text{C}$  was assumed as quite low, we shall have to expect a temperature of up to  $600^\circ\text{C}$  for

<sup>1</sup> Even if the suction gases are at first only at room temperature or, because of evaporation, lower, they are considerably preheated by the hot cylinder walls and by the mixture with remnants of hot combustion gases in the cylinder; the above figures are therefore not too high (*cf.* Ricardo, cited p. 507).

the latter part of the charge in the engine. It is clear from the data in an earlier chapter (pages 473ff.) that, under such temperatures, a lively reaction proceeds in the unburned mixture. In Figs. 222 and 223, we quoted Tizard and Pye<sup>1</sup> as well as Jost and Teichmann (page 474) on the induction time for auto-ignition at various temperatures determined by these men, especially for *n*-heptane and air. Since the measurements were carried out under adiabatic compression, they are directly comparable with engine conditions. As we can see, an approximate exponential connection exists between the period of induction and the temperature. We have extrapolated the measured values of Tizard and Pye to the higher temperatures, which is permissible for purposes of orientation. The induction periods for *n*-heptane are from about 400°C on, so short that operation with compression ratios of more than about 3:5 is out of the question with this fuel.<sup>2</sup> We shall see that practical determinations of knock values corroborate these conclusions (*cf.* the critical compression ratios, Table 112, page 555).

Even though the final pressures and temperatures actually reached in the compressed mixture will be lower than those given in Table 105 because part of the heat is imparted to the cylinder wall, they will, in general, still be high enough to make spontaneous reaction in the mixture, a factor not to be neglected. If this spontaneous reaction leads to auto-ignition before the spark occurs (*i.e.*, in general before compression is complete), the result is premature ignition; this should be prevented because of the premature and sudden increase in pressure.<sup>3</sup> Schematically the following picture presents itself (Fig. 240): The solid line shows the conversion with spark ignition through the progressing flame. Even under normal conditions of operation (Fig. 240*a*), there would be spontaneous conversion without an ignition spark, and it should not be neglected (approximately represented by the dot-dash curve 2\*). This conversion, however, takes place so slowly that it need not play any role in addition to the normal combustion. However, if spontaneous reaction sets in so quickly that it leads to rapidly progressing conversion

<sup>1</sup> TIZARD and PYE, quoted p. 472.

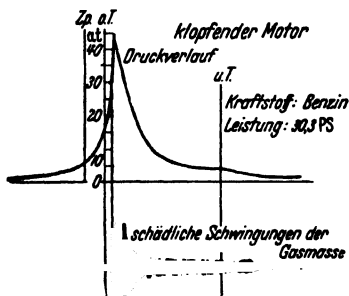
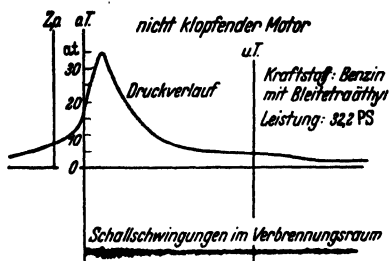
<sup>2</sup> Meanwhile Jost and Teichmann (cited p. 475; *cf.* also the detailed discussion of W. Jost, Paper read at the Convention of the German Academy of Aeronautical Research, Berlin, March, 1939, printed in *Schriften deut. Akad. Luftfahrtforsch.*, 1939) have succeeded in predicting quantitatively the occurrence of knocking in an experimental engine from auto-ignition behavior determined in the same engine.

<sup>3</sup> For practical operation, premature ignition in the homogeneous phase is almost out of the question, but it may occur at overheated parts of the wall, the spark plugs, etc.

\* Under these conditions, the conversion according to the dotted curve 2 would complete its course only if the piston were held in place at the end of the compression stroke. Otherwise the reaction about to take place can perhaps be stopped short by expansion and cooling of the gas.



ahead of the ignition spark (dash curve, Fig. 240a, 3), then there is premature ignition. Fundamentally, spontaneous reaction is calculable on the basis of facts and principles discussed in Chaps. VIII and XI (cf. the example on page 511) if the reaction rate of the mixture under consideration is known as to its dependence upon composition, pressure, and temperature.



$Zp$  = ignition point  
 $o.T.$  = upper dead center  
 $u.T.$  = lower dead center  
 nicht klopfender Motor = nonknocking engine  
 Druckverlauf = pressure variation  
 Kraftstoff: Benzin mit Bleitetraäthyl = fuel: gasoline with lead tetraethyl  
 Leistung: 32.2 PS = output 32.2 hp  
 Schallschwingungen im Verbrennungsraum = sound vibrations in the combustion chamber  
 klopfender Motor = knocking engine  
 schädliche Schwingungen der Gasmasse = harmful vibrations in the gas mass

FIG. 242.—Indicator diagram of normal and knocking combustion (abscissa = degree of crank angle); gas vibrations in the combustion chamber simultaneously recorded (Nielsen). (From v. Philippovich, p. 493.)

If the reactions (Fig. 240b) in the unburned gas were to proceed without spark ignition, according to the dash curve, while the solid curve again represents the conversion by the normal, undisturbed flame, then—in the absence of mutual influence—the total process would be represented as a superposition of the two by the dot-dash curve in Fig. 240b; i.e., after a normal initial phase, a suddenly increased conversion would follow toward the end. In reality, the reaction in the unburned gas will, of course, not proceed independently of the progression of the flame; because, through progression of the flame, the unburned remainder is further compressed and heated so that this effect can make itself strongly felt even when, without the flame, a strong conversion according to Fig. 240b is not observable. A conversion as just described would result in an indicator diagram approximately like the one given in Fig. 242. An initially normal pressure rise that is suddenly accelerated toward the end is exactly what has been observed in knocking of engines.

Maxwell and Wheeler have obtained experimental bomb photographs with simultaneous pressure data that correspond to knocking combustion. Under such conditions, knocking combustion can be obtained only if on the one hand the reaction chamber is very large so that there are small cooling losses and if on the other hand the last part of the

mixture has been compressed sufficiently by the previously burning charge. Maxwell and Wheeler used an explosion vessel of 15 cm diameter and 38 cm length, provided with a glass window. It is interesting that the addition of  $\text{Pb(eth)}_4$  to the mixture at  $15^\circ\text{C}$  hardly influences the course of knocking combustion of pentane; at best it accelerates it a

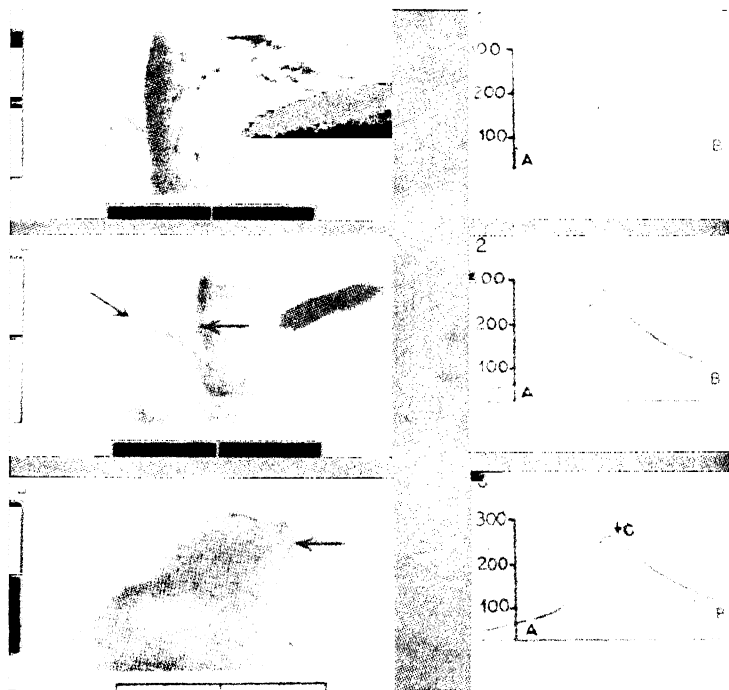


FIG. 243.—Flame pictures through a window in the engine (ignition, lower left; flame runs upward, film runs to the left). Below, hardly knocking; in the middle, weakly knocking; and above, strongly knocking combustion. At the right, corresponding pressure recordings, which show the pressure peaks in knocking. Since the window does not disclose the entire combustion chamber, knocking can appear in the pictures even after the flame has apparently traversed the entire combustion chamber (lower picture). (From Roseweiller and Withrow: *The Science of Petroleum*.)

little. If lead tetraethyl is allowed to decompose before introduction at  $\sim 300^\circ\text{C}$ , a completely nonknocking combustion results. This observation is in harmony with other experiences (cf. page 499). Figure 242 shows indicator diagrams of knocking and of normal combustion of an engine according to Nielsen.<sup>1</sup> The upper picture shows the process of combustion in normal combustion with only slight gas vibrations; the lower shows the variation of pressure with knocking combustion,

<sup>1</sup> NIELSEN, *Arch. tech. Messen*, **3**, 173 (January, 1936). Cf. PHILIPPOVICH, cited p. 503.

which is overlaid with strong gas vibrations that are separately recorded.<sup>1</sup>

Flame pictures of knocking combustion in the engine itself with synchronous pressure registration have been published by Rassweiler and Withrow.<sup>2</sup> Figure 243 shows three photographs of combustion, the first with very weak knock, the second and third with hard and very hard knock. Typical are the suddenly increased flame speed toward the end, the corresponding sudden rise in pressure in the indicator

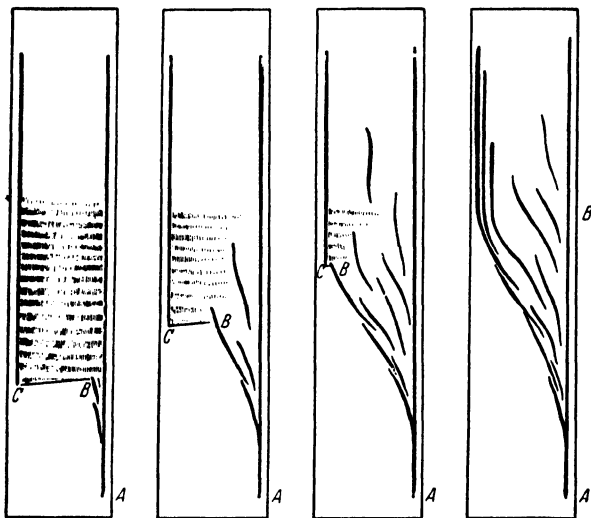


FIG. 244.—Schematic presentation of the course of the flame, observed by Duchêne (p. 504) in nonknocking (right) and (to the left) increasingly knocking combustion. Ignition at *A*; film movement downward; horizontal hatching = percussion waves with slight disintegration. (From Estradère, p. 457.)

diagram, and the percussion waves running back and forth in the burned gas, which we have become acquainted with in Chap. IV, pages 139ff. The "frequency" of the oscillating percussion waves, as is to be expected, agrees with the frequency of the vibrations registered piezoelectrically or otherwise in the indicator diagram. Rassweiler and Withrow have published<sup>3</sup> an especially good picture that reveals this. Deduction of the speed of knocking combustion is worth trying from Rassweiler and Withrow's picture; but, because of lack of sharpness of the flame front, it is uncertain. At all events, speed of knocking combustion is

<sup>1</sup> For observations of gas vibrations and their variations with the location in the combustion chamber, cf. especially Boerlage, Broeze, Driel, and Peletier, *Engineering*, **143**, 254 (1937); also Broeze, Driel, and Peletier, Paper read at the Convention of the Deutsche Akademie der Luftfahrtforschung, Berlin, 1939. For the basic principle, see the paper by E. Schmidt.

<sup>2</sup> RASSWEILER and WITHROW, *Ind. Eng. Chem.*, **23**, 769 (1931); **24**, 528 (1932); *Automotive Engr.*, **24**, 281, 385 (1934).

<sup>3</sup> Cf. "The Science of Petroleum," Vol. IV, Figs. 4 and 5b, p. 2915.

greater in order of magnitude than that of the normal flame, probably by a few hundred m/sec. Rassweiler and Withrow report 800 to 900 m/sec. There exists no compelling reason to assume for it a detonation speed of about 2 km/sec. Schnauffer<sup>1</sup> found the velocity of knocking combustion to be about 300 m/sec; Serruys gives 500 m/sec. All these data

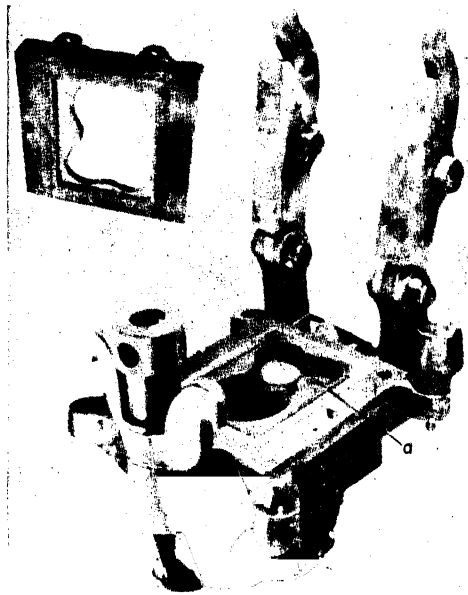


FIG. 245.—Experimental engine of Rassweiler and Withrow (p. 506) the combustion chamber of which is closed off by a quartz plate; cylinder viewed diagonally from above; at a valves and spark plug.

agree as well as we can expect in view of the uncertainty of the flame front in a turbulent mass of gas.

The analogous course of combustion can be obtained in a somewhat clearer form in a laboratory apparatus (Duchêne).<sup>2</sup> Since the original pictures are not available for reproduction, we reproduce a schematic representation by Estradère<sup>3</sup> (Fig. 244). Rassweiler and Withrow<sup>4</sup> made

<sup>1</sup> SCHNAUFFER, *SAE J.*, **34**, 17 (1934); also quoted p. 506; cf. Philippovich, cited p. 503.

<sup>2</sup> DUCHÊNE, M.R., Service technique et industrielle de l'aéronautique, *Bull. technique* 54, Paris, 1926. This publication contains studies concerning flame speeds under adiabatic compression without knocking. DUCHÊNE, R., *Pub. sci. tech. ministère air France*, No. 11, Paris, 1932; *Compt. rend.*, **186**, 220 (1928); **192**, 1633 (1931).

<sup>3</sup> ESTRADÈRE, SUZANNE, quoted p. 465.

<sup>4</sup> RASSWEILER, L.C., and G.M. WITHROW, *SAE J.*, **39**, 297 (1936); *Ind. Eng. Chem.*, **28**, 672 (1936). The cylinder used had a bore of  $2\frac{7}{8}$  in. and a stroke of  $4\frac{3}{4}$  in.; compression ratio 4.7:1. The quartz window was  $5\frac{1}{4}$  by  $4\frac{3}{4}$  in. in size and had to stand a pressure load of about 2.5 tons on its exposed surface. If the engine runs at

pictures of an actual engine whose cylinder head was closed by a quartz pane; they used a camera taking 5000 pictures per second. Rothrock and Spencer<sup>1</sup> got similar pictures. Withrow and Rassweiler used the arrangement shown by Fig. 245, which illustrates the complete development of the flame. For details of arrangements and of the optical method, we must refer to the original. Pictures of nonknocking and

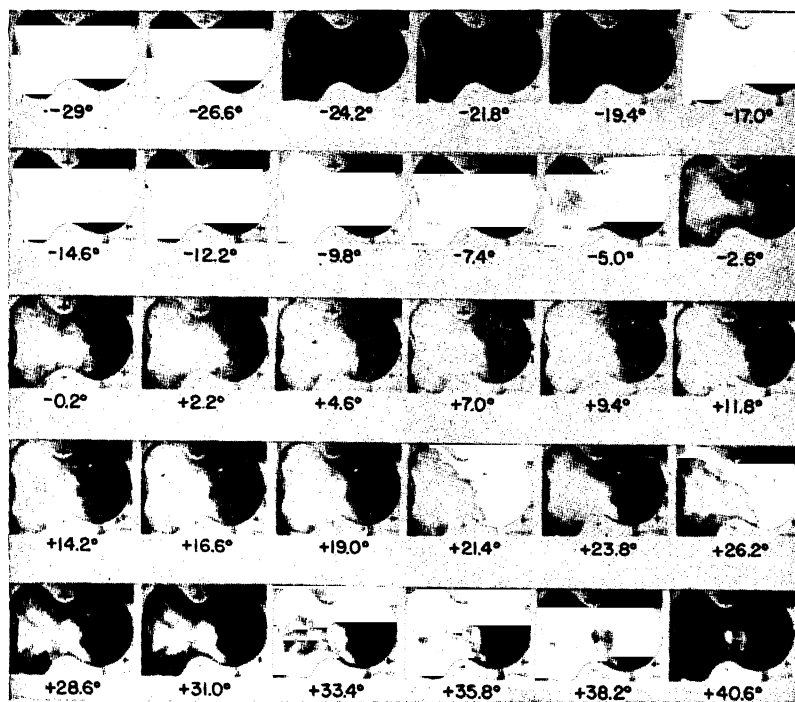


FIG. 246. - Slow-motion pictures of normal combustion from Rassweiler and Withrow: steady progression of the burning zone, which has traversed the entire combustion chamber at about  $+12^\circ$  crank angle; ignition  $23^\circ$  ahead of dead center. Afterglow of the burned gases.

knocking combustion thus obtained are shown in Figs. 246 to 248. These clearly show the steady progression of the split flame front in normal combustion (Fig. 246), as well as the almost instantaneous reaction of the remainder in knocking combustion (Figs. 247 and 248). The last series of knocking pictures also shows that the knocking reaction does not have to start at the flame front (*cf.* in that connection other experiences, page 522; the pictures of Duchêne, mentioned above,

2000 rpm and pictures are to be taken at each  $2.4^\circ$  of crank angle, an exposure time of only  $\sim 10^{-4}$  sec is called for, which requires a special optical arrangement.

<sup>1</sup> ROTHROCK and SPENCER, *NACA Rept.* 622, 1938.

show something similar). Moreover, it is shown that this auto-ignition in the unburned mixture does not emanate from hot places in the wall (this, of course, does happen also) by the fact that, in the series of six pictures of knocking combustion, this reaction started time and again in a different place. Such a reaction in the unburned gas can (probably because of higher temperature differences in the gas) proceed also in

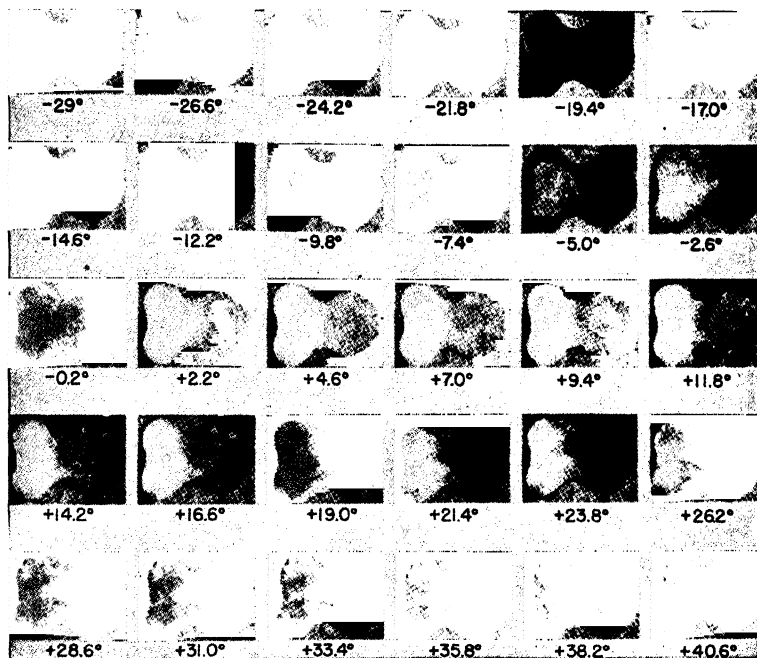


FIG. 247.—Pictures of knocking combustion. Up to  $-2.6^\circ$  crank angle the course is like that of normal combustion; at  $-0.2^\circ$ , ignition in the unburned mixture occurs removed from the flame front; it is followed by a very rapid reaction of the remainder. Already at  $+2.2^\circ$  everything is burned. (From Rassweiler and Withrow, p. 566.)

such a way that auto-ignition starts in one place but that, beginning from there, a new flame spreads normally (Serruys, quoted pages 531, 533, 535; Sokolik and Voinov, quoted page 531; Rothrock and Spencer, quoted page 516; Broeze<sup>1</sup>). The same can also take place from hot spots on the wall (spark plugs). What occurs then is an accelerated rise in pressure but no knocking (Serruys calls it "pseudodetonation"). In knocking combustion, the knock-reacting mixture remaining may under certain circumstances be compressed into a very small volume (because

<sup>1</sup> BROEZE, J.J., H. VAN DRIEHL, and L.A. PELETIER, Paper read at the Convention of the German Academy of Aeronautical Research, May, 1939; printed in *Schriften deut. Akad. Luftfahrtforsch.*, 1939.

of compression by the progressing flame), for which reason its reaction is not directly observable under certain circumstances. This may be the case in some of Rothrock and Spencer's pictures. Furthermore, through the turbulent gas currents, unburned parts may get behind the flame front and there be able to react only with knocking (*cf.* the phenomenon discussed on page 143).

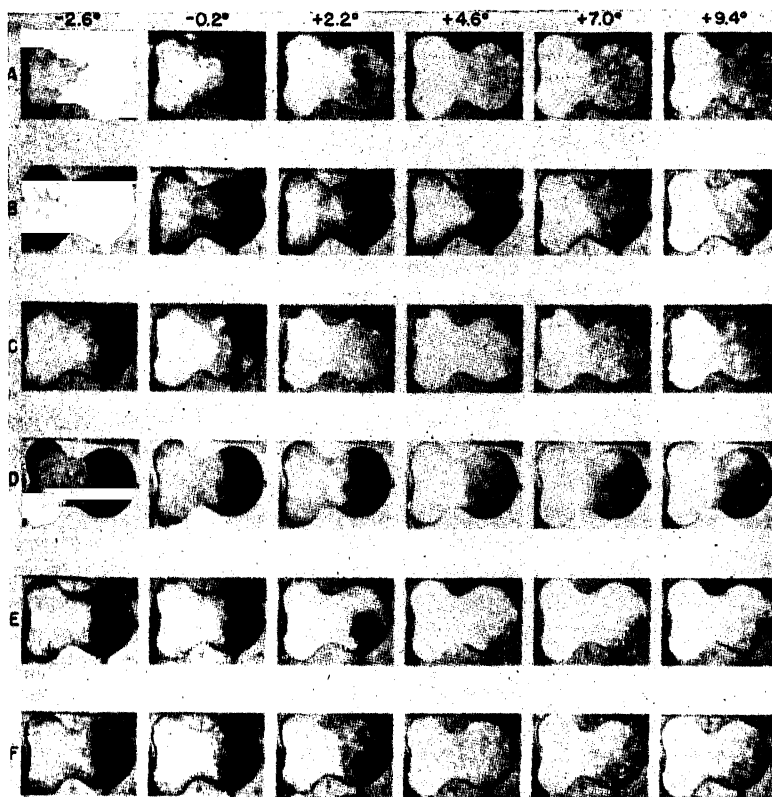


FIG. 248.—Six pictures of knocking combustion (A-F), which show that knocking occurs again and again in different places, sometimes in connection with the flame front, sometimes removed from it, and that it is therefore not caused by hot spots in the wall. (From Rassweiler and Withrow, p. 506.)

Finally, it has repeatedly been observed that, in knocking combustion, the intensity of the primary normal flame was strongly reduced<sup>1</sup> as the conditions of knocking combustion were approached (Duchêne, cited page 514; Rothrock and Spencer, and others). The cause of this phenomenon is not quite clear yet. Perhaps it is connected with the pre-reactions in the unburned gas; the spectroscopic findings of Rassweiler

<sup>1</sup> And that under certain conditions its velocity was reduced.

and Withrow in engines (pages 551ff.) can be quoted in support of this. Simultaneously, with progressing combustion, a stronger reillumination of the burned gases or, in regular knocking, shock waves can be observed. This reillumination can easily be interpreted as a consequence of compression in the burning of the remaining charge (cf. pages 148ff.), and it will be superfluous to assume the course of a further reaction behind the flame front, as Duchêne and Rothrock and Spencer suggest. Nevertheless, further attention should be paid to the phenomena that are not yet clear in all details.

The explanation of the knocking process has caused more difficulties than the discovery of the most effective antiknock compounds by Midgley and his collaborators.<sup>1</sup> It had long been recognized that the metallic knocking noise did not come from moving metal parts but was caused by the sudden pressure rise in the gas mass. It was harder to explain where the sudden pressure rise came from, however. Since, in contrast to normal flame propagation, the detonation wave is connected with a sudden rise in pressure, the suggestion that a knocking detonation occurred seemed natural enough. This view was held, for instance, by Midgley,<sup>2</sup> who distinguished himself in knock research. Although more recent research has—with one exception, cf. page 521—led to the result that knocking in engines is not a true detonation, the term “detonation” has been widely used in the literature (especially in English and American) to designate the knocking process. The word “detonation” is used there mostly in a metaphorical sense. What is common to knocking and true detonation is increased propagation velocity of combustion and therewith increased pressure rise as compared with ordinary combustion, and the formation of shock waves that oscillate in the burned gases with the speed of sound or faster. These are recognizable by vibrations in the indicator diagram and the associated reillumination of the burned gases due to compression. This is often observable toward the end of combustion behind the flame front even without marked knocking. The presence of detonation is contradicted by the fact that it has never been possible to get a detonation with the hydrocarbons in mixtures with air used in engine operation. Furthermore, a detonation wave would have to progress with a calculated speed of the order of magnitude of 2 km/sec, whereas the measurements in engines have resulted in values of between approximately 200 and 900 m/sec (cf. pages 513, 514). Those are, to be sure, extraordinarily high velocities, in fact ten times greater than those of normal combustion in engines and suffi-

<sup>1</sup> Cf. WILSON, R.E., *Ind. Chemist*, **29**, 239 (1937). MIDGLEY, T., JR., *Ind. Eng. Chem.*, **29**, 241 (1937).

<sup>2</sup> MIDGLEY, T., JR., and JANEWAY, *SAE J.*, **12**, 367 (1923). For a discussion of this question, cf. G.G. Brown and G.B. Watkins, *Ind. Eng. Chem.*, **19**, 366 (1927).



cient for an explanation of all phenomena observed in engine operation. This is still a long way from the velocities of a true detonation, however. Furthermore, a stationary detonation wave can, in general, proceed only in a tube of constant diameter (*cf.* Chap. V, page 187). Detonation disappears in passing from a narrow tube into a wider tube; whereas, conversely, in passing from a wide to a narrow tube, detonation is not impeded so long as the narrow tube is wide enough for a detonation to propagate in it at all.<sup>1</sup> For this reason, the geometric prerequisites for a true detonation are not fulfilled in an engine. On the other hand, the fact, known since Ricardo, that the shape of the cylinder head is essential in knocking might support the point that conditions that favor the occurrence of sudden pressure waves are favorable for knocking.<sup>2</sup>

We shall now discuss the only diverging observations according to which true detonations supposedly occur in engines, as presented by Sokolik and Voinov.<sup>3</sup> These authors, like Withrow and Boyd before them, made pictures of flames in an engine provided with a window. It was a specially constructed, one-cylinder engine, corresponding to an airplane engine (127·140 mm, 1.77 liter, with a roof-shaped combustion chamber and overhead valves with a spark plug at one end), with a top window of pyrex glass, 6 mm wide and 150 mm long, which was mounted in a somewhat conic piece of metal adjustable like a cock. As long as no pictures were taken, this cock was so adjusted that the window could not become covered with condensation. In comparison with the measurements made by Withrow and Boyd, as well as the experiments of Duchêne (which were made, to be sure, not in the engine itself, but with gases adiabatically compressed, as they would be in an engine), the arrangement of Sokolik and Voinov is better because pictures can be taken with a powerful lens 1:2 on a drum rotating up to 7000 rpm, corresponding to a linear speed of up to 60 m/sec. Consequently a better analysis and a quantitative determination of the occurring speeds is certainly possible insofar as the light intensities permit.

In knocking combustion, all the pictures of different experimenters appear like the ones in Fig. 244, with greatly increased flame speed toward the end, followed (perhaps) by a shock wave that is recognizable as a zigzag line in the picture. The determination of absolute velocity in the last part of the combustion is difficult, first because of the absence of analysis in the older pictures, but also because in this final combustion the intensity of the flame is not always sufficient. In the pressure wave that follows, the determination is under certain circumstances much

<sup>1</sup> *Cf.* in this connection, p. 574.

<sup>2</sup> Since heat conduction, turbulence, and length of the flame progression play an important role, it would be difficult to draw valid conclusions from this consideration.

<sup>3</sup> SOKOLIK, A., and A. VOINOV, *Tech. Phys. USSR*, **3**, 803 (1936).

better, allowing a satisfactory determination of speed of the order of magnitude of the velocity of sound in the burned gases. If a true detonation has occurred, the result is, as Sokolik and Voinov acknowledge, a picture about like Fig. 249, in which the film speed is much greater than in Fig. 244. The section at *D* corresponds to the actual detonation wave, which would have to have a velocity of  $\sim 2000$  m/sec, as it is indeed recognizable in a few of Sokolik and Voinov's pictures. In many pictures, however, this section is not at all recognizable; there are, rather, pictures like Fig. 250 where, to be sure, the primary flame and

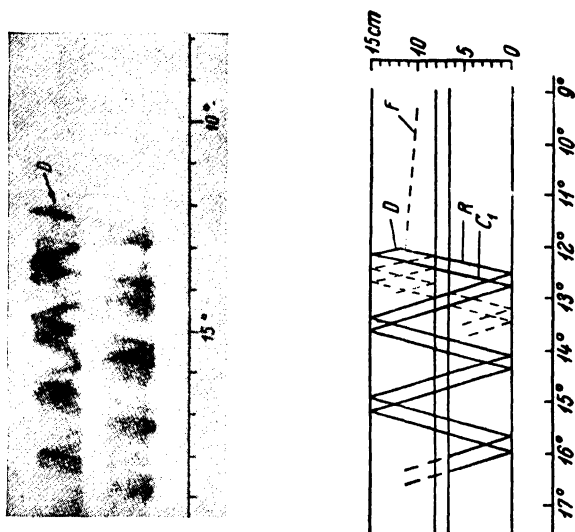


FIG. 249.—Picture of knocking combustion with great film speed. At the right, schematic representation of the picture: film movement from bottom to top; ° crank angle as time scale; flame *F* ran from right to left. According to the authors, detonation is said to have taken place at *D*; then reflected percussion waves follow. The "retonation wave" *R*, which ought to appear in case of a detonation and which has been sketched in, can probably not be recognized in the photograph itself. (From Sokolik and Voinov, p. 510.)

the shock wave following it are recognizable, but not the end of the primary flame which leads into the shock wave. Estradère (page 515), for instance, who publishes flame pictures made with Duchêne's apparatus, represents her pictures schematically (Fig. 244). Here we cannot possibly be dealing with a detonation; it must instead be a self-ignition of the unburned remainder. Otherwise the flame front could not run counter to the primary flame. Figure 251 has nothing to do with the phenomena under observation, but it shows auto-ignition very neatly, perhaps caused by a hot spot on the wall, in the unburned mass without knocking.

Among the pictures published by Sokolik and Voinov, a few seem to show detonation; most of them, to be sure taken with lesser drum speed,

correspond rather to the type shown in Figs. 244 and 250.<sup>1</sup> The pictures of Estradère and probably also those of Duchêne seem to correspond only to the type of Fig. 244. The situation, therefore, cannot yet be regarded as clear. Perhaps it is justified to consider the observations of Sokolik and Voinov for the time being as a borderline case occurring rarely. The pictures by Rassweiler and Withrow and by Duchêne had shown that the occurrence of shock waves is in general a consequence of knocking combustion.<sup>2</sup> Still the diagrams of Nielsen (page 512) show that, in the pressure diagram, vibrations can be proved to be present before reaching the point of

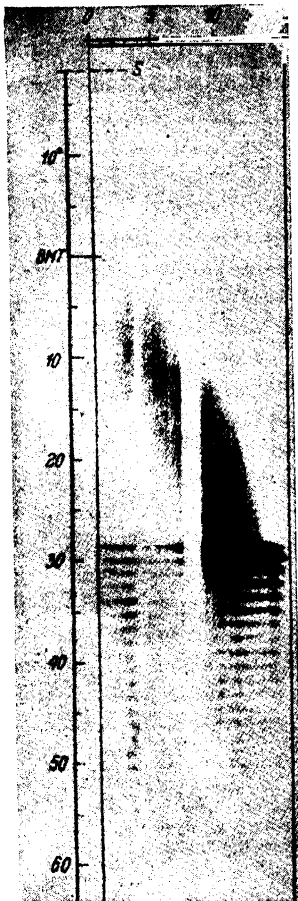


FIG. 250.—Picture of knocking combustion, with primary flame (ignition, upper left) percussion waves in the burned portion. (From Sokolik and Voinov, p. 510.)

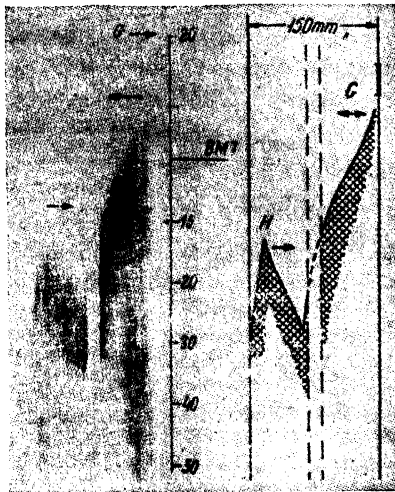


FIG. 251.—Picture of engine combustion by Sokolik and Voinov (p. 510), which shows auto-ignition in the unburned mixture (at *H* in the schematic presentation at the right) but without knocking.

maximum pressure.<sup>3</sup> This does not contradict what was said before, but it makes advisable the consideration of how far primary shock waves may

<sup>1</sup> BROEZE, DRIEL, and PELETIER especially point out possibilities of error in the pictures of Sokolik and Voinov, paper read at the convention of the German Academy for Aeronautical Research, Berlin, 1939.

<sup>2</sup> Cf. in this connection also BROEZE, DRIEL, and PELETIER, cited above; Jost, W., and Jost and TEICHMANN, cited pp. 511, 475.

<sup>3</sup> Also cf. pp. 138ff. about the origin of percussion waves and oscillations.

be responsible for the induction of knocking.<sup>1</sup> The author would like to assume that normally shock waves should be regarded as the secondary phenomenon and that their aid in the induction of knocking need be considered only in special cases.

Let it be said that, in spite of the great difference in the process of knocking, either by detonation or by auto-ignition of the unburned mixture, the theoretical and practical problem in both cases is still more nearly similar than we might at first assume. Since normally no detonation is observed in the mixtures of hydrocarbons and air, and since furthermore in the progress of combustion in cylindrical tubes a certain running length is required until actual detonation occurs with detonating mixtures, a pre-reaction would manifestly have to occur in the engine and would lead to intermediate detonating products. A possibility<sup>2</sup> of a pre-reaction might therefore exist which, under certain circumstances, would yield submolecular intermediate products in such concentrations that detonation would become possible. However, this would first have to be proved by special experiments and seems, for the time being, improbable. The essential thing in knocking, at any rate, is the pre-reaction. If knocking consists not of a detonation but only of an accelerated reaction<sup>3</sup> of the remaining gas, this too must be induced by a pre-reaction. The fact that the propagation speed is different in the two cases does not play a very important role, because it does not make much difference in engine operation and observable peak pressure whether the speeds of flame propagation are 10 or 100 times greater than in normal combustion, if only they are of the order of magnitude of the speed of sound or greater; for, under those circumstances, the combustion of the remaining part may be regarded as taking place practically under constant volumes (*cf.* pages 528ff.).

Figure 240 suggests two approaches to the elimination of knocking:

1. Diminution of the time available for knocking reaction, *e.g.*, through a moderate increase of normal combustion velocity,<sup>4</sup> so that combustion is already finished before the sudden conversion starts in the unburned part.
2. Deceleration of the reaction in the unburned gas, so that the final pressure rise does not occur.

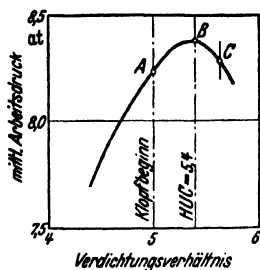
<sup>1</sup> The experiments of Rothrock and Spencer (*NACA Rept.* 622, 1938) contradict such an effect.

<sup>2</sup> *Cf.* SOKOLIK, A., and K. SHTSHOLKIN, *Acta Physicochim. URSS*, **7**, 581, 589 (1937); also Chap. V, p. 230.

<sup>3</sup> In "ideal knocking," a simultaneous auto-ignition of the entire remaining mixture would have to occur; this ignition will not occur simultaneously if irregularities of composition and temperature are present.

<sup>4</sup> In this, the influence of flame velocity on knocking becomes evident; we have pointed this out several times.

Suitable engine construction can lead to results in both directions. Regarding deceleration of reaction in the unburned part, chemical methods have been used. The former may at least be pointed out, even if we shall discuss only the latter in detail here.



(mittl. Arbeitsdruck = mean working pressure  
Klopfbeginn = beginning of knocking  
Verdichtungsverhältnis = compression ratio)

FIG. 252.—Mean working pressure as a function of the compression ratio in determining the highest useful compression ratio, HUC. (From *Giessmann*, p. 495.)

*Giessmann*, shows average working pressure as a function of compression ratio as obtained, according to *Ricardo* (cf. page 535), in the determination of the greatest usable compression ratio for the determination of knock values. Performance improves with slight, occasional knocking under increase of compression ratio, and it drops off with heavier knocking. The greatest usable compression ratio reached was used by *Ricardo* as a measure for the knock resistance of a fuel. As an example of the decrease in performance of an engine operating on a fuel with poor knock resistance ("octane numbers," to be discussed later, were used as a unit of measurement), we give Fig. 253 from *Philippovich's* summary, page 503. This shows that poor knock resistance does not manifest itself in performance at first but that a few minutes later a considerable decrease in performance can occur, which makes further operation of the engine impossible.

1. Acceleration of ordinary combustion through (a) turbulence, (b) shape of cylinder, (c) location of spark plug, and (d) size of cylinder and increase in rpm.

2. Deceleration of the reaction in the unburned part through increased cooling partly in consequence of turbulence, partly through cylinder shape, size, and wall material.

Knocking interferes with engine operation because of the high peak pressures and temperatures occurring and the simultaneous decrease in performance. Weak knocking need not as yet be connected with a decrease in performance; Fig. 252, according to

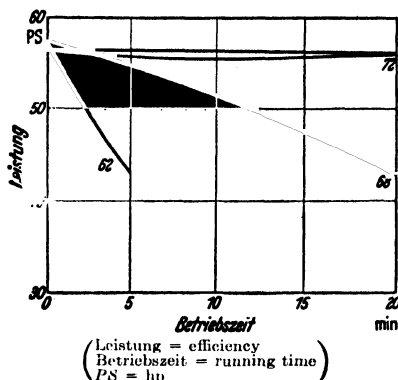


FIG. 253.—Decrease of engine efficiency with running time for sufficiently knock-resistant fuels (OZ 72) and not sufficiently knock-resistant fuels, OZ 62 and 68, Pontemoli. OZ = octane number. (From *Philippovich*, p. 493.)

Probably heavier knocking occurs only to the extent to which the engine heats up, since knocking must depend to a large degree on the temperature of the mixture. The average temperatures in the combustion chamber rise with increasing compression and knocking. The exhaust temperatures drop with rising compression,<sup>1</sup> which is favorable for the overheated exhaust valves. This is clear from the thermodynamic ideal process treated at the beginning and is directly understandable without calculations. If, under a higher compression ratio, the energy transformed into useful work increases, less energy must remain in the working substance; *i.e.*, therefore, the exhaust gases must become cooler.

**4. Essential Considerations in the Combustion and Knocking Process in Engines.**—In the following paragraphs of this chapter, we shall deal chiefly with the nature of the processes that cause knocking, with the difference in knock resistance of the various hydrocarbons, and with the possibilities of influencing knocking. Very interesting questions present themselves, however, even if we assume simply that knocking is a very quick reaction of a remaining part of the charge in the engine and investigate what results are produced.

We must for this reason first recall the conditions of normal combustion in the engine in the light of the general knowledge gained earlier (pages 148ff.). We have seen that, with combustion in a closed chamber, irregular temperature distribution, even when all heat-conduction effects are excluded, is fundamental, occurring in such a way that, after combustion is completed, the place from which combustion starts (*i.e.*, near the spark plug) shows the highest temperature, and the place last reached by the flame is the coldest. Temperature differences in this vary by hundreds of degrees. For calculations in engines, it is best to use a numerical procedure.<sup>2</sup> With a cylindrical combustion chamber divided into imaginary layers of equal depth, the procedure would be as follows: We presuppose the combustion velocity as being small in comparison with the speed of sound, so that complete pressure equalization always takes place, an assumption permissible for normal combustion. Furthermore, let us assume an ideal case in which during the combustion the piston is arrested in upper dead center, so that the total volume is constant. If the imaginary layers are chosen sufficiently thin, the combustion of every layer can be regarded as taking place under almost constant pressure. Each burning layer simultaneously expands and then compresses the unburned as well as the previously burned gas,

<sup>1</sup> Heat conversion during expansion is greater, too, in knocking operation; *cf.* Rassweiler and Withrow, *SAE J.*, **36**, 125 (1935); *cf.* in this connection also the theoretical considerations of E. Schmidt, Paper read at the Convention of the German Academy for Aeronautical Research, appearing in *Schriften deut. Akad. Luftfahrtforsch.*, 1939.

<sup>2</sup> *Cf.* in this connection G.G. Brown, *Chem. Rev.*, **22**, 27 (1938), where extensive bibliography is given; also G. Damköhler, *Jahrb. deut. Luftfahrtforsch.*, **2**, 62 (1938).

causing temperature changes in these other layers. If the heat of combustion and the specific heat are known, the temperature distribution can be calculated for each instant. We have reported it qualitatively for a similar case in Chap. IV, Fig. 107, for the initial, partial, and complete conversion. Spatially constant temperature always prevails in the unburned gases. Temperature drop prevails in the burned gases in the direction from the place of ignition. The mean temperature of the entire volume is not identical with the temperature that would prevail with even temperature distribution. Because of the temperature dependence of the specific heats, it is, like the pressure, somewhat lower than the corresponding values calculated for even distribution. For practical purposes, however, this difference, amounting usually to less than 1 per cent, may be neglected.

Calculation may be made by means of suitable thermodynamic tables.<sup>1</sup> As an example, we quote<sup>2</sup> the fact that, in an engine with  $\epsilon = 4.4$  and 80 per cent of the theoretical air, a temperature drop of  $\sim 350^\circ\text{C}$  was measured, whereas calculation (and for 85 per cent theoretical air) amounted to  $\sim 600^\circ$ . The difference between calculation and experiment can probably be explained (aside from the effect of cooling and turbulence) by the fact that combustion took place not under constant volume but over an extent of a  $40^\circ$  crank angle.

For an estimate of the temperature reached in the unburned mixture (whose temperature is of decisive importance in the occurrence of knocking), the following information may be of use. As already mentioned (page 240), there remains a discrepancy of at least  $\sim 160^\circ\text{C}$  within which lies the temperature calculated for the burned gas as compared with the one measured directly according to the line-inversion method.<sup>3</sup> This amount must have been brought about during combustion by cooling, which because of turbulence is many times greater than would be calculated for gases at rest. Since the unburned gases are much colder than the burned ones, the amount of their cooling must also be smaller than in the burned gases. A cooling of the unburned gases of the order of magnitude of  $\sim 50^\circ$  will have to be regarded as possible. Furthermore, the cooling of the burned gases also has an effect on the temperature reached in the unburned portion, since thereby the pressure, and thus the compression, of the unburned gases is lowered. For this

<sup>1</sup> For instance, the one of Hershey, Eberhard, and Hottel, *SAE J.*, (4), **39**, 409 (1936).

<sup>2</sup> RASSWEILER and WITHROW, *SAE J.*, **46**, 125 (1935). Concerning measurement and calculation of gas temperatures in Otto engines, cf. also M. Donescu, *Pub. sci. tech. ministère air* 69, 1935, with detailed references to literature. It is noteworthy that explosion temperatures rise in the order of hexane, heptane, iso-octane, cyclohexane, benzol; i.e., in the order of decreasing hydrogen content.

<sup>3</sup> HERSHEY, A.E., *Chem. Rev.*, **21**, 431 (1937).

reason, by the way, any local cooling has its effect on the entire volume of gas in a closed chamber, and we should not reason without qualification that no real drop in temperature had occurred in all regions that are too distant from the cold walls to be affected by direct heat conduction.

All these effects must be considered in passing judgment on temperature measurements with thermo-elements that give average temperatures over the entire work cycle.<sup>1</sup> The adiabatically compressed fresh gas reaches its highest temperature in the place farthest away from the spark that is reached last by the flame. Conversely, the burned gases show their highest temperature in the vicinity of the place of ignition. Temperature averages, therefore, hardly bring out the particular temperatures of interest in individual cases.

Brown also calculated pressures, volumes, and temperatures for the Otto cycle under consideration with uneven temperature distribution; the diagram reproduced in the original shows (as is to be expected) that, in the normal combustion process, efficiency is not noticeably decreased by this factor. It is quite different in knocking combustion, however. Regarding the nature of knocking, it is only presupposed in this that combustion in the knocking part of the charge takes place more quickly than its volume adjustment can take place. The question, therefore, of whether knocking is a true detonation, an instantaneous auto-ignition of the remainder of the charge, or a process somewhere between these two remains entirely open. For appraisal, Brown uses the following data<sup>2</sup> which appear to him sufficient to regard knocking as the combustion of the remaining part of the charge under constant volume. Normal combustion at 900 rpm required a crank angle of  $37^\circ$  or 0.0067 sec. Knocking combustion under the same conditions was completed in  $22^\circ$  of crank angle or 0.0041 sec. The normal combustion of the first half of the charge required the same time in both cases, approximately 0.0036 sec, so that for the knocking combustion of the remainder about 0.0005 sec was available.<sup>3</sup> From Rassweiler and Withrow's pictures, it is directly clear that the position of the burned gases has not changed during this knocking combustion and that, consequently, combustion has taken place under constant volume.

<sup>1</sup> Cf. BOERLAGE, BROZE, DRIEL, and PELETIER, *Engineering*, **143**, 254 (1937).

<sup>2</sup> RASSWEILER and WITHROW, *SAE J.*, **39**, 297 (1936).

<sup>3</sup> The time estimated by Brown for knocking combustion may probably be regarded as too long. Assuming that the "knock zone" extends over about 5 cm, 0.0005 sec would correspond to a speed of  $\sim 100$  m/sec. If combustion is to take place without volume change, however, its speed would have to be comparable with at least the speed of sound, i.e.,  $\sim 500$  m/sec; the required time would then be 0.0001 sec. That would tie in with Schnauffer's (cited p. 514) and Serruys's observations. Serruys (cited also p. 531), in an example of direct oscillographic pressure indication, gives the duration of the pressure rise during knocking combustion as  $\sim 3 \cdot 10^{-5}$  sec.



In the combustion of the last part of the charge, extraordinarily high peak pressures, whose measuring depends on the accidental position of the pressure-measuring element, must occur in places. Pressure instability must then spread with greater speed than that of sound as a shock wave that is many times reflected between the walls of the chamber and yields the usual picture of vibrations in the indicator diagram.<sup>1</sup>

An estimate of the possible peak pressures in knocking combustion is easily obtained. Assuming that at the end of compression the mixture is under pressure of about 8 atm, which rises because of combustion to about 40 atm, the last small particle of the charge before combustion would be under  $\sim 40$  atm. During combustion of the remainder at its own volume, a pressure rise of fivefold, a maximum pressure of 200 atm, would occur. This pressure peak, however, occurs only in an extremely small volume and must therefore soon "dissipate," so that it cannot have a harmful effect.

With stronger knocking, the instantaneously burning volume is larger; the initial pressure and the peak pressure are therefore a little lower. Nevertheless these are bound to have a harmful effect in the operation of the engine. Maximal pressure data result from theory as well as from direct measurements.

Brown (quoted page 526) calculated the diagram for the ideal process of the Otto cycle (Fig. 254) for knocking combustion under the assumption that the last third of the charge burns within its own volume. For details of the calculation, we must refer to the original. Here we reproduce only as much

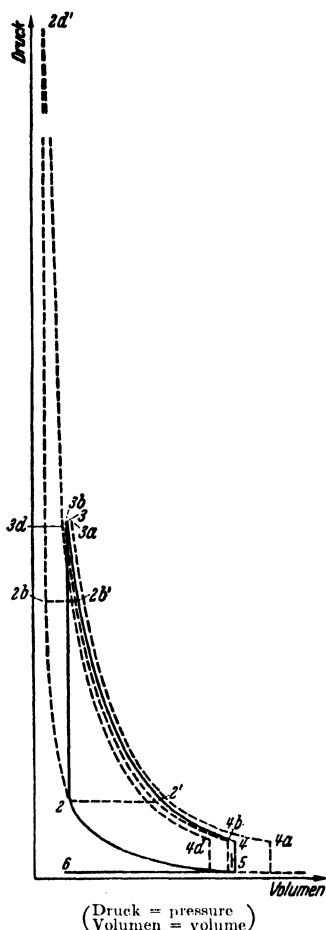


FIG. 254.—Diagram for knocking combustion. It is assumed that the last third of the charge burns in its own volume. 1, 2, 3, 4, 5, 6, solid line, average values for the total mixture. Dashed, specific values for *a*, the first part of the charge; *b*, last part of the normally burning charge; and *d*, of the remainder burning with knocking (smallest specific volume and highest pressure). (From Brown, p. 516.)

<sup>1</sup> The pressures measured in different parts of the combustion chamber must depend essentially on geometrical relations.

as is necessary for the understanding of the diagram.<sup>1</sup> The solid lines in the diagram represent the average values of the entire mixture, which are important in the calculation of performance and efficiency. Alongside them, drawn as dotted lines, are the specific values (volumes and pressures) of (a) the first part of the charge, (b) the last part, which burns normally, and (c) the part that burns with

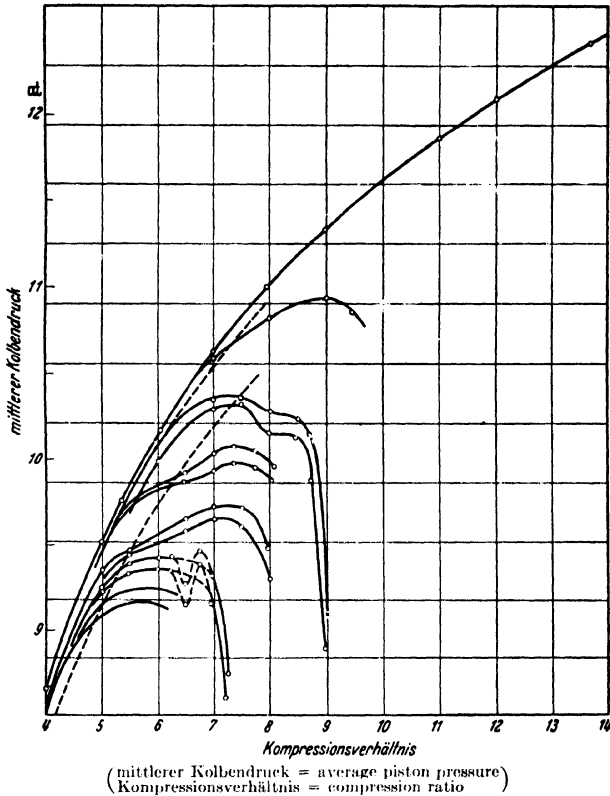


FIG. 255.—Variation in the output with the compression ratio for various gasolines. In knocking, the output drops after reaching a maximum. Upper curve for benzol. (Presentation from Brown, p. 516.)

knocking, for which the maximal pressure is about 2.65 times as great as it would have been with an even ending of the combustion. Brown's data in the cycle process refer to  $\epsilon = 6$ ; the peak pressure with knocking of one-third of the charge is calculated at above 70 atm. This high local peak pressure resulted in a decrease of the mean effective pressure and with it a decrease of performance. It is easy to see that this is

<sup>1</sup> Cf. also G. Damköhler, quoted p. 525.

qualitatively so. The gas from the region of superhigh pressure must flow to regions of low pressure; shock waves form, in which necessarily a part of the energy of the gas is present in the form of kinetic energy of the directed movement. Owing to the constancy of energy, the energy of the nondirected movement and with it the average pressure must diminish by this much. If the shock waves run in the direction of piston movement, a more exact consideration is called for.

INFLUENCE OF KNOCKING ON OUTPUT AND EFFICIENCY FOR  $\epsilon = 6$

|                                   | Normal | Knocking |
|-----------------------------------|--------|----------|
| Output, Btu <sup>1</sup> .....    | 475    | 450      |
| Efficiency, %.....                | 32.9   | 31.0     |
| Mean effective pressure, atm..... | 12.8   | 12.1     |

<sup>1</sup> British thermal units; since it is a matter of a comparison between normal and knocking operation, converting to the usual measure is superfluous.

Brown, for instance, calculates the above data for normal and knocking cycles. Solely because of the effects described, performance (and efficiency) decreases in knocking of one-third of the charge amount to almost 6 per cent.

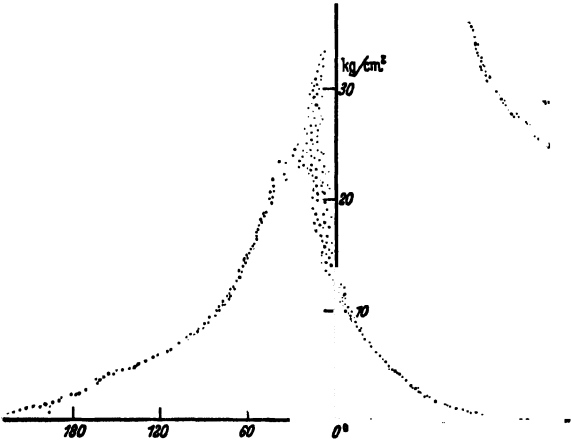


FIG. 256.—Farnboro diagram of normal combustion (time axis runs to the left; 0° = upper dead center). (From Serruys, *Aircraft Eng.*, 1938.)

Figure 255 represents the actual, measured decrease in performance (mean effective pressure) under increasing compression and initial knocking.<sup>1</sup> For the actual decrease in performance in the engine, not only will the variations of average pressures computed from the ideal process have to be considered; but it must also be kept in mind that,

<sup>1</sup> BROWN, cited p. 525, from G.G. BROWN, *Oil Gas J.*, **27**, 156 (1929).

because of knocking, the condition of the engine, especially the temperature of the individual parts of the wall, changes fundamentally; that, because of these changes, the process of combustion is further influenced for the worse; and that all these secondary effects can, under certain circumstances, bring about a much greater deleterious effect than can the entire primary performance decrease.

A number of the preceding considerations are verified by direct measurement.<sup>1</sup> The high peak pressures and gas vibrations (shock waves) following them are well known from many pictures; they also appear clearly in Serruys's experiments. Figure 256 reproduces a diagram of normal combustion obtained with the Farnboro indicator;

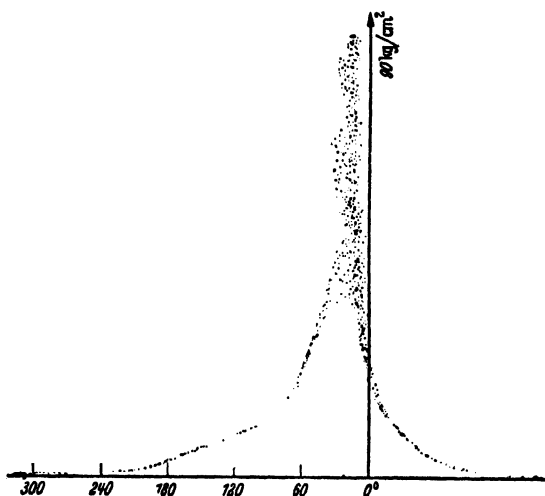


FIG. 257.—Farnboro diagram of knocking combustion. (From Serruys, p. 521.)

the maximum pressure is 32 atm, whereas (Fig. 257), in knocking combustion, peak pressures of over 90 atm occur.

The diagrams made with Serruys's optical indicator show more details. The pressure recording also depends on the place in the combustion chamber where the indicator has been installed.

As examples of light and medium-strong knocking we show one more diagram (Fig. 258), which clearly indicates extreme pressure variations in knocking and the milder gas vibrations following them. In this diagram, slight vibrations can be seen even before the beginning of knocking; these have been observed frequently, and often a special role has been assigned to them in the start of knocking. Especially

<sup>1</sup> For a systematic survey, cf. v. PHILIPPOVICH, A., *Z. Elektrochem.*, **42**, 472 (1936). SERRUYS, M., "Science aérienne," pp. 172ff.; *Aircraft Eng.*, **10**, 143 (1938).

after the experiments of Rothrock and Spencer,<sup>1</sup> who found no influence of artificially induced shock waves on the beginning of knocking, this assumption seems not generally applicable, even if occasionally such vibrations might be regarded as coeffective in inducing knocking. A combustion (similar to knocking) of small partial volumes that have got in or behind the burning zone<sup>2</sup> or an intensification of the vibrations (as was also discussed in connection with H. Schulze, page 142) could be held accountable for the vibrations appearing before actual knocking. The apparent frequency of the vibrations decreases during expansion, as is to be expected in consequence of temperature drop and volume increase. The speed of the shock waves under Serruys's conditions

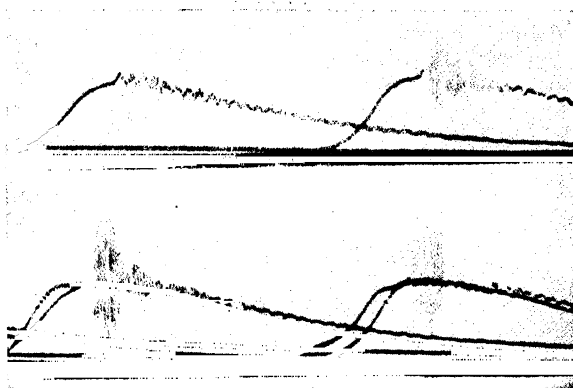


FIG. 258.—Inductor curves (Serruys indicator) of light and medium-heavy knocking (time axis runs left), which emphasizes the pressure peaks and gas vibrations. (From Serruys, p. 521.)

was  $\sim 800$  m/sec. Since shock waves of small amplitude propagate at a speed only slightly above that of sound, the determination of the speed of such waves (either natural or artificially induced) would also be a means of temperature measurement in the engine.

For the thermal demand occurring because of knocking, the following considerations of Serruys are valid:

a. Overheated places are not always identical with those which are normally hottest.

b. The position of the place of maximum heating is dependent on the location of the spark plug.

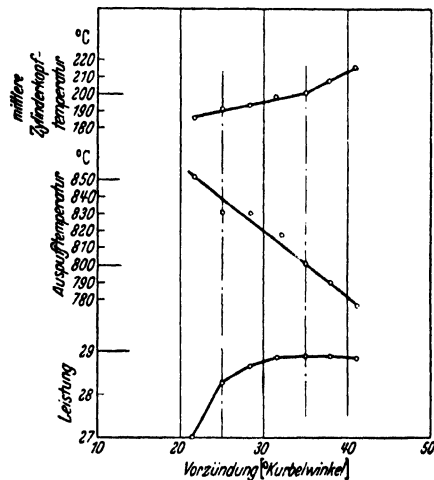
All this is to be expected after the preceding theoretical considerations. Although, during normal combustion, the burned gases become hottest in the vicinity of the place of ignition, in knocking they initially reach highest temperature in the part burning last and farthest away

<sup>1</sup> ROTHROCK and SPENCER, *NACA Rept. 622*, 1938

<sup>2</sup> Cf. the observation by H. Schulze, p. 144.

from the spark plug. The shock wave emanating from there, however, causes heating up in other places too. The wave effect time and again brings about a reheating of the gas portions near the walls, thus increasing heat conversion.

If the spark is advanced in an engine close to knocking condition, knocking will set in more easily. Even so, performance may increase with slight knocking; it always decreases in heavy knocking. Simultaneously the temperature of the exhaust gases drops, and the temperature of the cylinder head rises because of the more active heat conversion



(Leistung = output  
 Auspufftemperatur = exhaust temperature  
 mittlere Zylinderkopf-temperatur = average cylinder-head temperature  
 Vorzündung = advanced ignition  
 Kurbelwinkel = crank angle)

FIG. 259.—Variation in output, exhaust temperature and average cylinder-head temperature with advanced ignition (increasing advanced ignition corresponds to increasing knocking). (From Serruys, p. 521.)

already mentioned (Fig. 259). If knocking is caused not by advancing the time of ignition but only by a poor quality of fuel, a decrease of performance is noted from the start (Ricardo). Serruys (we shall discuss these matters later in connection with the reaction-kinetic considerations in the knocking process) stresses that clear relations can be reached only if all auto-ignition because of overheated spots in the cylinder is avoided. Figure 260 shows such an anomalous situation in which auto-ignition and knocking are simultaneously present. Knocking and auto-ignition may occur separately or together in the same combustion. By auto-ignition, we mean here the occurrence of ignition in any place of the unburned mixture, far from the flame front, mostly emanating from glowing spots in the wall; this will spread with normal velocity (in contrast

to knocking, which represents an almost instantaneous ignition of the entire remnant of the mixture). Since, however, even with auto-ignition in this sense an accelerated pressure rise is present, we should not be deceived into regarding this as knocking. Confusion of these two phenomena might under certain conditions be the cause of many discrepancies. Serruys,<sup>1</sup> in this sense speaks of "detonation" and "pseudodetonation."

Raising the temperature and pressure (overloading) of the intake air promotes knocking; we shall later refer to this (page 535). Let us

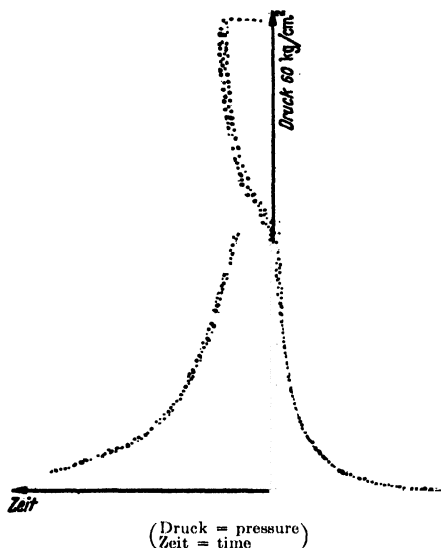


FIG. 260.—Anomalous indicator diagram with simultaneous auto-ignition and knocking. (From Serruys, p. 521.)

remark here that in general (*e.g.*, Serruys, quoted page 531; F.A.F. Schmidt<sup>2</sup>) the increase in knocking is interpreted as a consequence of the change of reaction conditions together with pressure. In this statement, certain reservations should probably be made. If the engine is overloaded, more energy, proportional to the overloading, is converted, more heat is given off to the walls, and the condition of the combustion chamber is changed. The walls are bound to become hotter and with them also the unburned gas. The heat conductivity, by the way, remains independent of pressure; the compressed gas therefore cools relatively less than the uncompressed gas, which in turn means a temperature rise of the gas in operation with overloading. Furthermore, dis-

<sup>1</sup> SERRUYS, M., *Compt. rend.*, **197**, 224 (1933).

<sup>2</sup> SCHMIDT, F.A.F., *Ver. deut. Ing. Forsch.* 392, 1938.

sociation of the burned gases is reduced by the pressure rise, while temperature correspondingly goes up, indirectly also in the *unburned* gases. The pressure effect observed is therefore actually predominantly a temperature effect.

We can conclude this indirectly from the experimental data of Serruys. He reports that the exchange of a cast-iron cylinder head for one of an aluminum alloy in many cases raises the performance to be obtained by about 15 to 20 per cent because of a diminished tendency toward knocking. The reason for this can only be the better heat conduction of the aluminum head and the lower wall temperature caused thereby. Serruys has checked this systematically and for this purpose first lined the cast-iron head with thin layers of aluminum, copper, and chromium; but operation was not essentially influenced by this. It is therefore not the nature of the surface that exerts this influence. In contrast, Serruys expected that roughing up of a sufficiently cooled wall, at least in the region of knocking, would probably have a good effect because of increased heat conduction. Experiments bear him out. Besides the cylinder heads already mentioned, one aluminum head with a striated surface was used. It was possible to obtain the following loads before knocking started:

|                           |           |
|---------------------------|-----------|
| Cast-iron head.....       | 8.415 hp  |
| Alpax head.....           | 9.53 hp   |
| Alpax head, striated..... | 11.925 hp |

The effect of the striated head can be explained only by increased heat conduction from the adiabatically compressed gas remainder. This is a proof for the fact that, with turbulence, heat loss through conduction plays a considerable role, although for static gases only comparatively small conduction would be calculated.<sup>1</sup> Since, however, *relative* heat loss in overloading must decrease inversely with the overload pressure, the mixture in overloading must be noticeably hotter just before burning (the effects may lie in the order of magnitude of 50°C); and this conditions to a large extent the stronger tendency toward knocking. Furthermore, pressure increase diminishes dissociation and thus increases temperatures.

**5. Measurement of the Knocking Process.**—Before considering the character of knocking, it seems in order to ask how knocking can be proved to exist and how the knock behavior of a fuel can be quantitatively characterized. If we are willing to put up with the uncertainties

<sup>1</sup> This, by the way, can be concluded from the heat given off to the cooling water. In connection with the preceding considerations, cf. also M. Serruys, *La combustion détonante dans les moteurs à explosion. Facteurs et incidences d'ordre physique et mécanique*, Pub. sci. tech. ministère air, 103. *Etude expérimentale de l'Allumage par Point chaud dans les Moteurs à Explosion*, Pub. sci. tech. ministère air, 115.



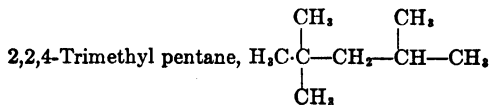
that are entailed in any subjective observation, the ear is the simplest indicator.

Ricardo was the first to build an experimental engine with variable compression ratio and by means of this to determine through increase of the compression ratio the instant when knocking is initiated for each fuel (for data concerning Ricardo's experimental engine, *cf.* H.R. Ricardo, cited page 507). The highest useful compression ratio (HUCR) determined in this manner is not only specific for the engine used (another ratio results for other engines), but even with the same engine it depends to a considerable extent on the condition of the engine. For that reason, all conditions of operation like rpm, temperature of the cooling water, preheating of mixture, time of ignition, and carburetor adjustment must be accurately fixed. Even then it is difficult to obtain absolute values independent of the momentary condition of the engine. Instead of being expressed by means of a quantity relative to the engine (compression ratio), as a rule the knock quality of a fuel is nowadays expressed in terms of comparison with a mixture of two standard fuels which yields under equal conditions in the same engine equally strong knocking. Accidental influences of the engine are thus to a large extent excluded.

Following the suggestion by Edgar,<sup>1</sup> *n*-heptane and iso-octane have been accepted. *n*-heptane has a very low and iso-octane<sup>2</sup> a very high knock resistance. Both are easily obtainable in pure form and have, besides, similar physical characteristics, especially almost identical boiling points (*n*-heptane 98.4; iso-octane 99.3°), so that no differences may enter into engine operation from that source. The *octane number* of a fuel is that iso-octane content (in per cent by volume) of an *n*-heptane-iso-octane mixture which shows the same knock behavior as the fuel being investigated, determined under standard conditions in a standardized test engine.

The CFR engine of the American Cooperative Fuel Research Committee is usually employed as the test engine; lately the IG testing engine<sup>3</sup> has also been used. The CFR engine has a displacement of 610 cm<sup>3</sup>, and its compression ratio can be continuously varied from 4 to 12 during operation. The CFR method is applied in various ways which differ by the prescribed conditions of operation. The original *research* method had

<sup>1</sup> EDGAR, G., *Ind. Eng. Chem.*, **19**, 145 (1927).



<sup>3</sup> For more detailed data, *cf.* W. Giessmann, *Z. Ver. deut. Ing.*, **80**, 833 (1936); also J.M. Campbell, and A. Boyd, "The Science of Petroleum," Vol. IV, pp. 3056ff.; also Nash and Howes, "The Principles of Motor Fuel Preparation and Application."

the most lenient conditions: temperature of cooling water 100°C, no preheating of mixture, 600 rpm. The CFR *engine* method, revised in the interest of better agreement with the results of practical engine operation, operates with 900 rpm, the same cooling-water temperature, but mixture preheating to 149°C. There are other modifications, but we shall not go into them here. In the CFR engine, the "bouncing-pin" indicator indicates knocking; it is a pin fastened to a membrane set in motion by the shock of knocking. The membrane is connected with the combustion chamber of the engine, and the whole instrument is so adjusted as not to react to normal combustion pressure. The bouncing pin closes two contacts at the upper end of the indicator, and a current flows through a system of resistance wires. The temperature of these wires is measured with a thermo-element and serves as a measurement for the knocking strength, not as absolute measure but as a relative measure for the adjustment of the fuel to be compared with the same reference fuel of the same knocking strength. If the knock behavior of all fuels did not change in the same manner under different conditions of operation, the knock value of a fuel would not depend on the assumed operating conditions. Since in reality it is so dependent, it follows that different fuels can be very differently influenced.

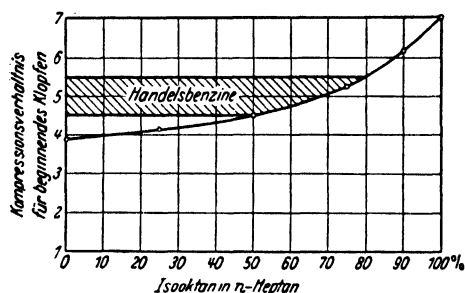
As a clue for the relation between octane number and compression ratio in initial knocking, which, because it is a physical datum, is of greater interest here than the technically more important octane rating, we give in Fig. 261 the compression ratios for iso-octane-heptane mixture, obtained by the more exacting CFR method (data according to Campbell and Boyd). The original *research* method, in terms of which many measurements that we shall have to use later are stated, results in compression ratios about one unit smaller with lower octane ratings.

An absolute measure would be desirable for characterizing the behavior of individual fuels. To a certain extent, the critical compression ratio furnishes it, for (aside from cooling losses) it permits a calculation of compression pressure and temperature at which knocking starts and thus permits the establishing of relations to otherwise known characteristics of hydrocarbons. Since, however, it depends on the specifically chosen engines as well as on the conditions of operation (temperature of cooling water and thus cylinder temperature, suction temperature, rpm, and suction pressure—atmospheric air pressure—moisture content), such data are never directly transferable to another engine.

Even the CFR engine method does not represent an ideal procedure for the determination of knock characteristics, but it has to a certain extent satisfied practical requirements for the standardization of fuels.

Note in the graph (Fig. 261) of the critical compression ratios of heptane-iso-octane mixtures that, in the small octane numbers, increase

in critical compression ratio for the unit of the octane number is much smaller than for high octane numbers. Measured in critical compression ratio, octane numbers do not represent a uniform scale, and the gain in knock resistance in the octane calibration 90 to 100 is several times that in the 0 to 10 bracket. Campbell *et al.*<sup>1</sup> also state critical compression ratios for a number of other fuel mixtures. In their data, it is notable that the increase of the critical compression ratio of *n*-heptane by the addition of a certain moderately large quantity of another more knock resisting fuel is not always proportional to the knock resistance of this fuel in pure form; *e.g.*, according to these figures, pure alcohol is less knock resisting than benzol, but nevertheless 20 per cent alcohol increases the



(Kopfsverhältnis für beginnendes Klopfen = compression ratio for beginning knocking)  
(Handelsbenzine = commercial gasolines)

FIG. 261.—Compression ratio for beginning knocking for *n*-heptane-iso-octane mixtures.  
(From Campbell and Boyd, *CFR Engine Method*, p. 527.)

critical compression ratio more than 20 per cent benzol. Presupposing that the rule of mixture holds true—which is not quite so—we could calculate from the octane number of the mixture a “mixture octane number” for the added substance, which in this case would, of course, be greater for alcohol than for benzol (and for both less than 100, at least under the research method). The peculiarities of individual fuels in mixtures will be taken up in detail later.

It is generally known that, by a small addition of certain substances, antiknock compounds, knock behavior can be essentially improved. This fact is of just as great practical importance as it is for the theoretical understanding of the phenomena. The influence of the antiknock substances, whose most typical and effective representative is lead tetraethyl,<sup>2</sup> depends essentially on the nature of the fuel to which they are added; their effectiveness does not increase with increasing addition but beyond a certain point yields only diminishing returns. That too is of fundamental importance.

<sup>1</sup> CAMPBELL, LOVELL, and BOYD, *SAE J.*, **26**, 163 (1930).

<sup>2</sup> Cf. MIDGLEY, T., JR., cited p. 502.

Metal compounds like  $\text{Pb(eth)}_4$  and  $\text{Fe(CO)}_5$ , if used as knock preventives, can have added undesirable effects on engine operation which can be overcome to a certain extent. For this, reference is made to the literature in question.<sup>1</sup>

**6. Processes Preceding Knocking.**<sup>2</sup>—Almost all experiments and theoretical considerations support the fact that the pre-reaction of the unburned gases is decisive. Experiments in engines show this most directly. There are two methods for gaining an insight into what occurs in the unburned gas after compression. Through special valves installed in engines for this purpose, samples from the cylinder can be withdrawn at certain times, and their compositions can be determined by analysis. The advantage of this method consists in the fact that as a matter of principle any substance that forms can actually be detected. The disadvantage is that the samples obtained may be different from those present in the cylinder and that, when the flame is progressing, it is difficult to take a sample consisting exclusively of unburned mixture.

The second method—proof of reaction products by their absorption spectra made possible even during operation through a special window—has the advantage that no interference with the course of the reaction takes place and that the spectrum can be studied in a part of the chamber which the flame has not yet reached and at an exactly defined time. The disadvantage, of course, is that only such substances can be determined which show characteristic absorption spectra with sufficient clarity in an easily accessible spectral region. Actually only formaldehyde has been proved in this manner to exist in an engine, but even this suffices for certain conclusions.

Of the material that deals with the analysis of gas samples from the cylinder, we want to discuss especially that of Egerton, Smith, and Ubbelohde<sup>3</sup> because it is the latest and the most reliable.

Egerton, Smith, and Ubbelohde carried on a very careful investigation of the combustion process in the engine itself. For this purpose, a Delco knock-testing engine of 76 mm bore and 127 mm stroke was especially prepared. At the side of the cylinder head away from the

<sup>1</sup> NASH, A.W., and D.A. HOWES, "The Principles of Motor Fuel Preparation and Application," London, 1935.

<sup>2</sup> Cf. also PELETIER, L.A., S.G. VAN HOOOSTRATEN, J. SMITTENBERG, and P.L. KOOYMAN, *Chaleur et ind.*, January, 1939; also the papers of A. Egerton as well as by Broeze, van Driel, and Peletier, read at the Convention of the German Academy for Aeronautical Research, Berlin, 1939. Peletier and his collaborators have furnished direct proof that slow hydrocarbon combustion and knocking reaction are the same chemical process by demonstrating the processes corresponding to cold flames in an engine.

<sup>3</sup> EGERTON, A., F. SMITH, and A.R. UBBELOHDE, *Phil. Trans. Roy. Soc. London*, **234**, 433–521 (1935); bibliography *ibid.*

spark plug, a threaded hole for the bouncing-pin indicator was provided at a distance of 89 mm from the spark plug. Into this hole a sampling valve was inserted, especially constructed and similar to the one used by Withrow, Lovell, and Boyd.<sup>1</sup> The sampling valve was water-cooled so as to preclude further reaction of the gas sample in it. The cooling-water exit temperature was held to 40°C to avoid as much as possible a condensation of reaction products. The valve lift amounted to only 0.0025 mm. For details of the valve manipulation, we must refer to the original source. A gas quantity of only 0.27 cm<sup>3</sup> was taken per engine revolution. The duration of valve opening varied between 10° and 15° of crank angle in the early stage of compression and in a later stage of expansion up to approximately 2° of crank angle at the instant of maximum pressure, corresponding to an opening of the valve of  $\sim \frac{1}{1800}$  sec at 600 rpm. Through the utilization of such brief openings of the valve, it was possible to take samples at exactly determined times of the cycle. Earlier detailed analyses of gas samples had been made only by Lovell, Coleman, and Boyd;<sup>2</sup> but, since the opening of the valve had been too long, no definite conclusions were obtained. Withrow, Lovell, and Boyd used a valve<sup>3</sup> giving much shorter openings, but only oxygen consumption was analyzed.

Table 106 gives the C and H content of the benzene or benzol used by Egerton. Furthermore Shell gasoline No. 1 with 8 cm<sup>3</sup> ethyl fluid per gallon, *i.e.*, 4.4 cm<sup>3</sup> Pb(eth)<sub>4</sub> per English gal, or 1 per cent, was used. Ethyl fluid is a mixture of about 35 per cent ethylene dibromide;

TABLE 106.—COMPOSITION OF THE FUELS INVESTIGATED BY EGERTON

|               | Shell No. 1<br>% by weight | Benzol |
|---------------|----------------------------|--------|
| Carbon.....   | 85.68                      | 91.30  |
| Hydrogen..... | 14.32                      | 8.70   |

the latter serves to remove lead in the form of volatile lead bromide from the engine so that it causes no trouble, especially on the exhaust valves, in the form of metal or oxide. Each fuel was investigated with four different throttle openings with constant rpm and ignition. With gasoline No. 1, a wide range of operational conditions resulted:

Throttle opening:

|           |                                       |
|-----------|---------------------------------------|
| 6°.....   | <i>No knocking</i>                    |
| 7½°.....  | <i>Slight, occasional knocking</i>    |
| 9°.....   | <i>Regular, moderate knocking</i>     |
| 10¼°..... | <i>Extraordinarily heavy knocking</i> |

<sup>1</sup> WITHROW, L., LOVELL, and BOYD, *Ind. Eng. Chem.*, **22**, 945 (1930).

<sup>2</sup> LOVELL, COLEMAN, and BOYD, *Ind. Eng. Chem.*, **19**, 373 (1927).

<sup>3</sup> WITHROW, LOVELL, and BOYD, *Ind. Eng. Chem.*, **22**, 945 (1930).

For each throttle opening and each fuel, the mixture composition was adjusted to maximum performance. The measured performance is shown in Table 107.

As long as the engine does not knock, the performances with different fuels differ but little. With heavy knocking, a considerable decrease occurs in Shell gasoline without lead. In each case at different times, gas samples were taken under the same operating conditions; these were first analyzed for CO, CO<sub>2</sub>, and O<sub>2</sub>. Some samples were also analyzed for H<sub>2</sub>, and between 0.7 and 2.4 per cent hydrogen was determined. For the values themselves, we must refer to the original; but we shall give here some data that are important for the comparison between the individual fuels, namely, the "inclination of the oxygen curves," *i.e.*, the percental decrease of the oxygen content (in reference to the entire gas quantity) per degree of crank angle, and thus a measurement for the speed of conversion (Table 108).

TABLE 107.—OUTPUT WITH VARIOUS FUELS AND THROTTLE POSITIONS  
(FROM EGERTON, SMITH, AND URBELOHDE)

| Throttle opening<br>degree | Shell No. 1,<br>watts | Shell No. 1 + lead,<br>watts | Benzol,<br>watts |
|----------------------------|-----------------------|------------------------------|------------------|
| 6                          | 204                   | 205                          | 207              |
| 7½                         | 281                   | 286                          | 290              |
| 9                          | 335                   | 340                          | 345              |
| 10¼                        | 352                   | 399                          | 400              |

TABLE 108.—SLOPE OF THE OXYGEN CURVES (FROM EGERTON; *cf.* THE TEXT)

| Throttle opening<br>degree | Slope of the oxygen curve for |              |        |
|----------------------------|-------------------------------|--------------|--------|
|                            | Shell                         | Shell + lead | Benzol |
| 6                          | 0.616                         | 0.616        | 0.600  |
| 7½                         | 0.848                         | 0.848        | 0.800  |
| 9                          | 1.167                         | 1.120        | 1.037  |
| 10¼                        | 1.930                         | 1.170        | 1.073  |

It is noticeable that the inclination in the case of benzol is consistently somewhat less than with other mixtures. With pure Shell gasoline and heavy knocking, it is especially great. Withrow, Lovell, and Boyd (quoted page 540) had found that the oxygen content decreased rapidly with heavy knocking. The ratio

Inclination of the oxygen curve for pure Shell gasoline  
Inclination of the oxygen curve for Shell gasoline + lead

is especially revealing for this:

| Throttle Adjustment                        | Ratio Above |
|--|-------------|
| 6° (no knocking with Shell).....           | 1.00        |
| 7½° (slight, occasional knocking).....     | 1.00        |
| 9° (continuous, moderate knocking).....    | 1.04        |
| 10¼° (extraordinarily heavy knocking)..... | 1.65        |

Egerton and his collaborators tried to calculate from these data approximate values for the average flame velocity, which rises from about 5.81 m/sec at 6° throttle adjustment to about 10 m/sec at 10¼°, and which is about 10 per cent greater for knocking Shell gasoline than for Shell with lead or benzol but, at any rate, does not change to any considerable extent, thus confirming other results.<sup>1</sup>

The analyses for aldehydes and peroxides are even more interesting than the above results, since they refer not to final reaction products but rather to intermediate products, which are more likely to permit conclusions concerning the mechanism of reaction. In order to obtain useful analysis values quickly, drops of the individual reagents must be exposed under standard conditions to the stream of gas. The time necessary for producing the reaction serves as a measure for the concentration. For the details of the method, we refer to the original. To demonstrate the presence of aldehydes, Schiff's reagent was used; for peroxide, a solution of potassium iodide, hydrochloric acid, and starch in distilled water. Sensitivity was standardized in a suitable manner. The conclusions that Egerton and collaborators draw are as follows:

1. A certain combustion takes place in the knocking zone before the flame reaches the sampling valve.
2. In this precombustion, aldehydes form up to a concentration of about 1 in 150, at the moment when the flame reaches the valve.
3. Peroxide-like substances were formed in a concentration of up to 1 in 10,000; they seemed to disappear before the flame reaches the valve.
4. The concentration of these "peroxides" increases with increasing knocking.
5. Benzol apparently produced no such peroxides.
6. Pb(eth)<sub>4</sub> decreases the formation of aldehydes and peroxides, an indication that it slows down pre-reaction.
7. Addition of aldehydes (up to 10 per cent acetaldehydes)<sup>2</sup> does not increase the peroxide concentration or the knock tendency; hydrogen behaved in the same way.

These investigations were discussed in detail because they show the possibilities and limitations of a direct analysis of the combustion

<sup>1</sup> Cf. WITHROW and BOYD, *Ind. Eng. Chem.*, **23**, 539 (1931). SCHNAUFFER, *Z. Ver. deut. Ing.*, **75**, 455 (1931).

<sup>2</sup> In higher concentrations (20 per cent), an increase in knocking occurs.

process in the engine and because they are methodologically of basic importance.

More detailed investigations concerning the nature of the occurring peroxides (*cf.* the original publication for particulars) yield the following results: The peroxides found consist for the most part of  $\text{NO}_2$ . The maximum values in the curves are due to two conditions: the presence of small quantities of sulphur compounds which form  $\text{SO}_2$  and prevent the separation of iodine in the droplets; and the deficiency of oxygen in the burned gases so that it cannot react with  $\text{NO}$ , into which  $\text{NO}_2$  is decomposed in the flame. Finally  $\text{NO}_2$  is also removed by the vapors of unsaturated compounds.  $\text{NO}_2$  forms very clearly and early, when the average gas temperatures are still quite low so that possibly the proximity of the hot exhaust valves is responsible for its formation.<sup>1</sup> In addition, the participants in the reaction must affect its inception. On the whole, the presence of  $\text{NO}_2$  seems to be of only secondary importance in knocking. Organic nitrites, to be sure, have the tendency to cause knocking, but nitrogen dioxide itself does not.

It seems that higher aldehydes, if they occur, are very quickly disintegrated into formaldehyde; this agrees with earlier experiments.<sup>2</sup> The results of Egerton are essentially in agreement with the spectroscopic results of Rassweiler and Withrow, namely, that formaldehyde is formed during pre-reaction. To be sure, Rassweiler and Withrow find appreciable quantities of formaldehyde only in knocking combustion; whereas Egerton and collaborators prove aldehydes also at other times, only, to be sure, in small concentrations. It is certain that formaldehyde occurs with knocking combustion in especially high concentration without being itself responsible for the knocking.

That aldehydes as such are not responsible for knocking was again investigated<sup>3</sup> in an arrangement that permitted operation of the engine on every second cycle. Samples for analysis could thus be taken with as well as without ignition. Formaldehyde and higher aldehydes were analyzed separately. Aldehydes occurred even in the cycle without ignition, although in smaller concentration. The concentration reached in the aldehydes lay mostly between  $10^{-3}$  and  $10^{-4}$  (molar fraction, referred to the entire mixture in the cylinder). Benzol yielded especially few aldehydes, iso-octane only little formaldehyde but mainly higher aldehydes.

<sup>1</sup> Probably we are dealing with a catalytic reaction, for gold-plating of the exhaust valve decreased the  $\text{NO}_2$  concentration (UBBELOHDE, DRINKWATER, and EGERTON, *cf.* p. 543).

<sup>2</sup> EGERTON, A., and L. M. PIDGEON, *Proc. Roy. Soc. London, A*, **142**, 26 (1933).

<sup>3</sup> UBBELOHDE, A. R., J. W. DRINKWATER, and A. EGERTON, *Proc. Roy. Soc. London, A*, **153**, 103 (1936).



If 10 per cent acetaldehyde is added to benzene, no noticeable knocking occurs; 0.005 per cent acetyl peroxide causes knocking in the fuel, but with 10 per cent acetaldehyde apparently less than 0.005 per cent acetyl peroxide is formed. For knocking, the acetaldehyde portion in the combustion chamber would have to amount to more than  $4 \cdot 10^{-3}$ . The engine could be operated on pure formaldehyde (in contrast to acetaldehyde) without knocking. The aldehydes formed in the engine are therefore by no means the reason for knocking and the occurrence of peroxides. Hardly any relationship exists, either, between formation of aldehydes and knock tendency of a hydrocarbon.

The preceding investigations are of special importance with regard to the so-called "peroxide theory of knocking." Several authors, first Callendar<sup>1</sup> and Moureu and Dufraisse, concluded that organic peroxides were responsible for knocking. The occasion for this was the proof of peroxide-like substances in the exhaust gases of engines and in experiments concerning slow oxidation of fuels. The theory in its original form (namely, that easily decomposing organic peroxides are formed in such concentrations that their explosion decomposition causes the knocking) was pretty well discredited on the basis of general reaction-kinetic experiences. The theory in its later form, however (namely, that peroxide-like intermediate products occur in the course of a chain reaction, leading perhaps to a chain-branching) has much in its favor; cf. the preceding chapter, pages 488ff. To be sure, according to Egerton, it is not possible to give analyses from the engine itself as proof of this. This should not be surprising, for it must be said that it is fundamentally very improbable that active intermediate products of a reaction can be proved analytically afterward in noticeable concentration. The fact that an intermediate product is highly active in general precludes a lengthy existence, just as, vice versa, a long existence (*i.e.*, proof in the reaction products in greater concentration) permits the assumption that these compounds have not been active as intermediate products in reaction.

From general experiences with the mechanism of hydrocarbon combustion, there is no doubt of the fact that knocking is a chain reaction that can be greatly accelerated by certain additions as well as prevented by the antiknock substances. Experiences in engines, too, can hardly be interpreted differently. To the former substances belong organic nitrites (amyl nitrite), ozone, and alkyl peroxide.<sup>2</sup> These, in very small

<sup>1</sup> CALLENDAR, *Engineering*, **123**, 147, 182, 210 (1927). MOUREU and DUFRAISSE, *Compt. rend.*, **184**, 29 (1927). MOUREU, DUFRAISSE, and CHAUX, *Ann. office nat. des combust. liquides*, **2**, 253 (1927).

<sup>2</sup> CALLENDAR, H.L., *Engineering*, **123**, 147, 182, 210 (1927). HOLMES, M., *Nature*, **133**, 179 (1934). BROOKS, D.B., *J. Ind. Petroleum Tech.*, **19**, 835 (1933).

concentrations,<sup>1</sup> even as low as 1%, can increase knocking in concentrations which in the case of antiknock substances like  $\text{Pb(eth)}_4$  suppress it.<sup>2</sup>

Ubbelohde and Egerton<sup>3</sup> undertook to investigate in detail the course of organic peroxides in knocking. The following are the types of peroxides<sup>4</sup> which enter into consideration:

|  |                              |
|--|------------------------------|
| $\text{R}-\text{O}-\text{O}-\text{H}$  | alkyl hydroperoxide          |
| $\text{R}-\text{O}-\text{O}-\text{R}$  | dialkyl peroxide             |
| $\text{CH}_2\text{OH}-\text{O}-\text{O}-\text{CH}_2\text{OH}$  | dihydroxy alkyl peroxide     |
| $\text{R}-\text{O}-\text{O}-\text{CH}_2\text{OH}$  | monohydroxy alkyl peroxide   |
| $\text{R}-\text{O}-\text{O}-\text{CHOH}-\text{R}$  | dialkyl monohydroxy peroxide |
| $\text{R}-\text{CHOH}-\text{O}-\text{O}-\text{CHOH}-\text{R}$  | dialkyl hydroperoxide        |
| $\begin{array}{c} \text{O}-\text{OH} \\   \\ \text{R} \\    \\ \text{O} \end{array}$                         | acyl peroxide (peracid)      |
| $\begin{array}{c} \text{R}-\text{HC}-\text{CH}-\text{R} \\   \quad \quad   \\ \text{O}-\text{O} \end{array}$ | alkylidene peroxide          |

As representatives of this group, the following substances were produced: diethyl peroxide, monoethyl hydrogen peroxide, hydroxy methyl acetyl peroxide, acetyl peroxide, and amylene peroxide. The analytical proof of these peroxides was carefully investigated; for details we refer to the original.

The fact that organic peroxides are effective "knockers" had been pointed out previously by various authors.<sup>5</sup> Because of the quantities necessary for exact measurements of these substances, experiments were made by spraying peroxidic products in gasoline solution into the suction air of the engine during operation of the test engine with Shell gasoline.

The results are contained in Table 109. Diethyl peroxide seems to be an even more effective proknock substance than amyl nitrite, and approximately 2 per cent is necessary for the same effect that 30 per cent ether produces. Acetaldehyde was again ineffective. When the same experiments were made with the engine running on ethyl gasoline, 1.5 per cent  $(\text{C}_2\text{H}_5)_2\text{O}_2$  produced no audible effect, although the number

<sup>1</sup> Referring to fuel quantity.

<sup>2</sup> MIDGLEY, T., JR., *Ind. Eng. Chem.*, **16**, 890 (1924). EGERTON, A.C., *Nature*, **119**, 427 (1927). TAYLOR, H.S., *Nature*, **119**, 746 (1927).

<sup>3</sup> UBBELOHDE, A.R., and A.C. EGERTON, *Phil. Trans. Roy. Soc. London*, **234**, 433 (1935).

<sup>4</sup> Cf. in this connection Rieche, A., "Alkylperoxyde und Ozonide," Dresden and Leipzig, 1931.

<sup>5</sup> EGERTON, A., and A.R. UBBELOHDE, *Nature*, **133**, 179 (1934).

of revolutions fell off by 10. Apparently the proknock influence of peroxide and the antiknock influence of the lead approximately compensate for each other.

TABLE 109.—INFLUENCE OF ATOMIZED GASOLINE-PEROXIDE MIXTURES IN THE INTAKE AIR ON THE KNOCKING BEHAVIOR OF A TEST ENGINE (FROM UBBELOHDE AND EGERTON)

| Atomized mixture   | Influence on the number of revolutions | Influence on knocking  |
|--|--|--|
| Gasoline alone.....  | -10                                    | Reduces the knocking   |
| 30% (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O <sub>2</sub> in gasoline.....  | —                                      | Intensive knocking; stopped the engine   |
| 6% (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O <sub>2</sub> in gasoline.....   | -25                                    | Violent knocking   |
| 3% (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O <sub>2</sub> in gasoline.....   | -25                                    | Strong knocking  |
| 1.5% (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O <sub>2</sub> in gasoline..... | -15                                    | Noticeable increase in knocking  |
| 30% Ethyl ether in gasoline.....   | -20                                    | Same effect as about 2% (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O <sub>2</sub> |
| 3.4% Amyl nitrite in gasoline....  | -20                                    | Same effect as 30% ethyl ether   |
| 0.5% Amyl nitrite in gasoline....  | —                                      | No effect  |
| 30% CH <sub>3</sub> CHO in gasoline.....   | -10                                    | Reduces the knocking   |

Strong perhydrol (with 30 per cent H<sub>2</sub>O<sub>2</sub>), when sprayed into the suction air, also had the tendency to increase knocking. An estimate of the maximum molar fraction was about  $6 \cdot 10^{-4}$ .

In comparison with this, diethyl peroxide, sprayed in a 1 per cent solution, results in distinct knocking when the molar fraction concentration is only about  $1.6 \cdot 10^{-5}$ . This estimate agrees with the result that the engine, when operating on gasoline with 0.1 per cent diethyl peroxide, shows a decided increase in knocking. Alkyl peroxide is therefore about forty times more effective than H<sub>2</sub>O<sub>2</sub>.

From this, it follows that it is useless to try to test for peroxide in engines with the usual reagents, since the peroxide concentration necessary for knocking lies mostly below the threshold of sensitivity of these reagents. The results of the following table show the effect of the additions on various fuels, pure cyclohexane and ethyl gasoline.

It is very clear then that lead tetraethyl counteracts the peroxides. Acetaldehyde does not cause knocking, as we have already seen, unless it contains acetyl peroxide. Butyraldehyde peroxide and amylene peroxide do not seem to be effective proknock agents.

The susceptibility of the knocking quality of fuels to proknock agents is very variable, according to the nature of the fuel. Addition of 14 per cent amyl nitrite (corresponding to a molar fraction of  $2 \cdot 10^{-4}$  in the cylinder gases) produced loud knocking in gasoline, hexane, and amylene. In the case of cyclohexane (with readjusted throttle), heavy knocking, with benzol, ethanol, and acetone, only a slight influence was

TABLE 110.—INFLUENCE OF ATOMIZED SOLUTIONS OF VARIOUS MATERIALS IN THE INTAKE AIR ON THE KNOCKING BEHAVIOR OF TWO DIFFERENT FUELS (FROM URBELOHDE AND EGERTON)

| Fuel           | Atomized solution   | Throttle position | Effect on number of revolutions | Effect on knocking                              |
|----------------|---------------------|-------------------|---------------------------------|---|
| Cyclohexane    | —                   | —                 | —                               | No knocking                                     |
| Cyclohexane    | 3% Diethyl peroxide | —                 | —20                             | Loud knocking                                   |
| Cyclohexane    | 3% Amyl nitrite     | —                 | —15 ÷ 20                        | Loud knocking (somewhat less)                   |
| Ethyl gasoline | —                   | 9                 | —                               | No knocking                                     |
| Ethyl gasoline | 3% Diethyl peroxide | 9                 | —15 ÷ 20                        | Occasional very light knocking                  |
| Ethyl gasoline | 3% Amyl nitrite     | 9                 | —15 ÷ 20                        | Occasional light knocking                       |
| Ethyl gasoline | —                   | 10¼               | —10                             | No, or very light, knocking                     |
| Ethyl gasoline | 3% Diethyl peroxide | 10¼               | —10                             | Continued moderate knocking                     |
| Ethyl gasoline | 3% Amyl nitrite     | 10¼               | —10                             | Continued moderate knocking (somewhat stronger) |

produced, or none at all. The difference in sensitivity may point to a difference in the length of the occurring reaction chains; *cf.* pages 553ff.

Furthermore, an attempt was made with improved methods to determine organic peroxides in the engine in addition to NO<sub>2</sub>. It was successfully shown that actually small quantities of organic peroxides were present in the unburned gases just before knocking started, in concentrations corresponding to the added peroxides under artificial induction of knocking. Thus it is shown that no experimental findings oppose a reasonable peroxide theory of knocking, in which peroxide-like substances are assumed as unstable intermediate products. On the contrary, this assumption is very probable.

**7. Investigations on Antiknock Substances.**—Egerton and Smith<sup>1</sup> have also investigated the influence of antiknock substances. It was already well known<sup>2</sup> that undecomposed Pb(eth)<sub>4</sub> does not inhibit carbon combustion but even promotes it under certain circumstances. When the Pb(eth)<sub>4</sub> was first decomposed or oxidized at about 300°, however, it hindered oxidation. These observations do not contradict the antiknock property of Pb(eth)<sub>4</sub>, which, with a few exceptions, had

<sup>1</sup> EGERTON, A., and F.L. SMITH, quoted p. 540 and pp. 517ff.

<sup>2</sup> MAXWELL, G.B., and R.V. WHEELER, *Ind. Eng. Chem.*, **20**, 1041 (1928); *cf.* also p. 498. EGERTON, A.C., and L.M. PIDGEON, *J. Chem. Soc.*, 1932, pp. 661, 676; *cf.* also LORENTZEN, *Z. angew. Chem.*, **44**, 131 (1931).

been observed generally; for in the engine the temperature conditions toward the end of the compression stroke are always such that  $\text{Pb(eth)}_4$  can decompose.

Berl<sup>1</sup> had found that atomized metal as well as colloidal lead added to the fuel slows down oxidation but that colloidal lead oxide does not. The discrepancy between this and other findings, according to which lead is effective in the presence of oxygen, might be explained by the degree of dispersion of the colloids used.

Egerton and Gates<sup>2</sup> had already found earlier that the vapors of potassium and thallium are very effective in raising the flash point of gasoline. These investigations were extended. For this purpose, in place of a sampling valve, an additional inlet valve was installed in the engine, through which various vapors, either in a nitrogen or an air stream, could be injected into the engine. The metals were kept in a heated metal container, through which the gas was drawn by suction. In these experiments, it was found that potassium and thallium vapors are extremely effective in the suppression of knocking.

Potassium was injected in a nitrogen stream. Thallium was also at first conveyed in a nitrogen stream, but in so doing only a slight antiknock effect was noticed, which increased enormously when 15 per cent air was mixed with the nitrogen.<sup>3</sup> In this case, thallium was found eleven times more effective than the same quantity by weight of tetraethyl lead. Potassium was about four times more effective than the same quantity by weight of lead. Since the vapor in contact with the hot air in the cylinder is certainly rapidly oxidized, the earlier conclusions of Egerton and Gates were corroborated, according to which an antiknock substance, in order to be effective, must be in a condition of incipient oxidation. The same method could not be used with metallic lead, because of its low vapor pressure. Selenium and tellurium were also found quite effective, selenium somewhat more so in an oxygen-containing gas than in nitrogen; tellurium was equally effective in both. Sodium, cadmium, zinc, iodine, and sulphur were found to be ineffective. It is especially striking that sodium is ineffective, in contrast to potassium. Iron carbonyl was effective only when introduced into the engine as such; when allowed to decompose previously, it was ineffective.<sup>4</sup> Aniline

<sup>1</sup> BERL, E., K. HEISE, and K. WINNACKER, *Z. physik. Chem.*, Sec. A, **139**, 453 (1928). BERL, E., and K. WINNACKER, *Z. physik. Chem.*, Sec. A, **145**, 161 (1929); **148**, 36, 261 (1930).

<sup>2</sup> EGERTON, A., and GATES, *Rept. Aeronaut. Research Comm. London*, 1079 (1926).

<sup>3</sup> Since oxygen is always present in the engine for the oxidation of metals, the effect of the oxygen in this case might consist of preventing the formation of larger droplets of metal.

<sup>4</sup> That might again be connected with the degree of distribution of the decomposition products.

was found to be one-thirtieth as effective as the same quantity by weight of  $\text{Pb}(\text{eth})_4$ . Ethyl iodide vapor was almost two-thirds as effective as the same quantity by weight of aniline. It is strange that iodine is ineffective in view of the finding of Midgley,<sup>1</sup> in whose fundamental

TABLE 111.—EFFECTIVENESS OF VARIOUS ADDITIONS AS ANTIKNOCK REMEDIES (FROM EGERTON)

| Substance                 | Method  | Relative effectiveness on the basis of weight   | No. of mols of combustible mixture to 1 mol of anti-knock at the same anti-knock effectiveness as 1 cm. <sup>3</sup> $\text{Pb}(\text{eth})_4$ gallon | Remarks  |
|---------------------------|---|---|---|--|
| Lead or lead tetra-ethyl. | Introduced as $\text{Pb}(\text{eth})_4$ with gasoline | —   | 365,000   | —  |
| Thalium (680°C) ..        | Metal container                                       | 11 times as effective as lead   | 3,950,000   | Introduced with air  |
| Potassium (200–400°).     | Metal container                                       | 4 times as effective as lead  | 275,000   | Introduced with nitrogen   |
| Selenium .....            | Metal container                                       | 0.067 times as effective as lead  | 74,300  | Little greater effect in the presence of $\text{O}_2$ than without |
| Tellurium (580°) ..       | Metal container                                       | 0.014 times as effective as lead  | 6,300   | White precipitate ( $\text{TeO}_2$ )                               |
| Lead tetraethyl...        | U tube (in place of a metal container)                | $\frac{1}{8}$ as effective as when introduced with gasoline                               | 45,600  | Forms $\text{PbO}$ at 375°C  |
| Aniline .....             | U tube (in place of metal container)                  | 0.019 times as effective as lead<br>0.031 times as effective as $\text{Pb}(\text{eth})_4$ | 3,170   | —  |
| Ethyl iodide .....        | U tube (in place of metal container)                  | 0.012 times as effective as lead<br>0.017 times as effective as $\text{Pb}(\text{eth})_4$ | 3,150   | —  |

Ineffective: Na, Cd, Zn,  $\text{I}_2$ , and Sn.

<sup>1</sup> MIDGLEY, T., JR., *Ind. Eng. Chem.*, **14**, 894 (1922).

investigations concerning antiknock substances iodine was about the first to be found, but it is in agreement with earlier experiments by Egerton and Gates.<sup>1</sup>

The conclusions of this investigation agree with those arrived at earlier by Egerton: (1) that the antiknock substance must be oxidized, (2) that it must be present as molecularly dispersed as possible, and (3) that it should be capable of existence in several stages of oxidation. It corresponds to this, that several oxides, stable even in higher temperatures, are known of lead, thallium, and even of potassium ( $K_2O_4$  and  $K_2O_3$ ), but not of sodium.

As was shown in part in the preceding chapter, many parallels exist between ignition behavior and knock behavior of substances that are useless for quantitative data, however, because (especially when the determination of the ignition point is done in such a manner as to let the fuel drip into an aerated, heated vessel) the influences of the walls are very strong and the pressure conditions deviate radically from those in the engine.<sup>2</sup> Thus, under certain circumstances, observations may result that are contradictory even qualitatively; *e.g.*, diethyl peroxide raises the flash point of hexane instead of lowering it;  $NO_2$  lowers the ignition point of hydrocarbons without having any marked influence on knocking; aldehydes can lower the ignition point of hydrocarbons

EFFECTIVENESS AS PROKNOCK SUBSTANCE (IN CONCENTRATION OF  $10^{-5}$ ) AND CHEMICAL STRUCTURE (FROM A.R. UBBELOHDE)

| Effective   | Not Effective   |
|---|---|
| $R-O \begin{smallmatrix} \vdots \\ \vdots \\ \vdots \end{smallmatrix} O-R$  | $RCH-CH_2$<br>$\begin{smallmatrix}   &   \\ O & -O \end{smallmatrix}$ |
| $R-O \begin{smallmatrix} \vdots \\ \vdots \\ \vdots \end{smallmatrix} OH$   |   |
| $HO \begin{smallmatrix} \vdots \\ \vdots \\ \vdots \end{smallmatrix} OH$  | $RCH-CO$<br>$\begin{smallmatrix}   &   \\ O & -O \end{smallmatrix}$   |
| $RC \begin{smallmatrix} \diagup O \\ \diagdown \end{smallmatrix} O \begin{smallmatrix} \vdots \\ \vdots \\ \vdots \end{smallmatrix} OH$ |   |
| $RCH(OH) \cdot O \begin{smallmatrix} \vdots \\ \vdots \\ \vdots \end{smallmatrix} OH$   | $CH_3-NO_2$   |
| $RO \begin{smallmatrix} \vdots \\ \vdots \\ \vdots \end{smallmatrix} NO$  | $C_6H_5 \cdot NO_2$   |
| $RO \begin{smallmatrix} \vdots \\ \vdots \\ \vdots \end{smallmatrix} NO_2$  |   |

<sup>1</sup> EGERTON, A., and GATES, *J. Inst. Petroleum Tech.*, **13**, 244 (1927).

<sup>2</sup> This is partly true even for the very interesting and careful measurements of Townend and collaborators.

For this reason, it will never be possible to classify fuels absolutely with an ignition value tester (as in Jentsch's attempts), even if the phenomena observed are interesting in detail and may be of practical use with careful evaluation.

without essentially influencing knocking; selenium has a stronger effect in raising the ignition point of gasoline than  $\text{Pb(eth)}_4$ , while exerting only a slight antiknock influence.

Ubbelohde<sup>1</sup> points out that all such peroxides and similar substances (nitrites) have a knock-inducing effect that can fall into two fractions at an O—O or an O—N bond, although substances where that is not possible do not induce knocking, either. This would again be a confirmation of the assumption that knocking is a chain reaction taking place in the unburned mixtures. Substances of the type of ethylene oxide are therefore ineffective.

**8. Spectroscopic Investigations in Engines.**—For the photographing of absorption spectra, Rassweiler and Withrow<sup>2</sup> used a test engine with two quartz windows opposite each other (but removed from the spark plug) through which the light of a continual source (tungsten-filament light or underwater spark) penetrated. The knocking zone was especially observed, i.e., a place that was located only 0.48 cm from the wall but removed from the spark plug.

From the pictures, it is clear that it is possible to identify formaldehyde. From this, an interesting number of facts result: When the engine does not knock, no formaldehyde is detected; on the other hand, the absorption ascribed to formaldehyde increases with increasing knocking. It makes no difference how the knocking is caused, by changing the composition of the mixture, especially making an over-rich mixture lean; by advancing the spark; by preheating the mixture; or by decreasing the rpm. Thus formation of formaldehyde and, simultaneously, knocking are favored first by producing a mixture that is more capable of reaction, second by a rise in temperature, and—in the other cases—by prolonging the available time (which is almost a trivial cause). It should by no means be concluded that the formaldehyde is the compound responsible for knocking; but what follows with certainty is that knocking occurs only when a certain pre-reaction, in which formaldehyde is possibly only a by-product, has taken place in the compressed mixture. The fact that there may be conditions in which formaldehyde is present but no knocking occurs is in favor of this assumption.

Results obtained with additions that induce or suppress knocking are also very striking. If knocking is induced by the addition of isopropyl nitrite, formaldehyde occurs especially distinctly; if knocking is suppressed by the addition of aniline, formaldehyde concentration is reduced; but, when knocking is suppressed by the addition of  $\text{Pb(eth)}_4$ , a noticeable quantity of formaldehyde still is in evidence.

<sup>1</sup> UBBELOHDE, A.R., *Z. Elektrochem.*, **42**, 468 (1936).

<sup>2</sup> WITHROW, L., and RASSWEILER, G.M., *Ind. Eng. Chem.*, **25**, 923, 1359 (1933); **26**, 1256 (1934); **27**, 872 (1935).



On the whole, these experiments show that knocking is very closely connected with pre-reactions but that the process should by no means be thought of as a simple one, that especially the occurring formaldehyde could be a good reagent for the pre-reaction but that it is not to be regarded as the agent originating knocking.

The same authors have made a further careful investigation of the effect of  $\text{Pb(eth)}_4$  on absorption in front of the flame front in the engine.<sup>1</sup> The following results should be emphasized: When knocking is suppressed by  $\text{Pb(eth)}_4$ , absorption of atomic lead, but not of lead oxide, is observed. The conclusion drawn by the authors that, with suppression of knocking,  $\text{PbO}$  is converted into  $\text{Pb}$  (*i.e.*, has an oxidizing effect) does not sound quite cogent (because the absorption of molecules is usually much weaker than that of atoms); but it nevertheless does not sound improbable. It is well known from experience that  $\text{Pb(eth)}_4$  is effective not as such but only after decomposition.<sup>2</sup>

Furthermore they found that, even if the concentration of formaldehyde is not decreased by  $\text{Pb(eth)}_4$ , the absorption is diminished below  $3000 \text{ \AA}$ . Obviously the concentration of an absorbing compound is decreased there; perhaps this compound plays a direct role in the knocking mechanism—in contrast to formaldehyde. In agreement with this is the fact that intentional addition of formaldehyde up to concentrations resulting in absorptions comparable with those observed in knocking does not cause knocking or an increase of continuous absorption below  $3000 \text{ \AA}$ . This statement agreed essentially with Egerton's investigations concerning the absorption of heated hydrocarbon and air mixtures,<sup>3</sup> in which a continuous absorption on the part of organic acids and peroxides was found, to be sure, mostly in short-wave ultraviolet. Their formation did not take place when  $\text{Pb(eth)}_4$  was added.

Besides absorption spectra of the unburned gases, emission spectra of the burned gases also permit some conclusions. Chapters VII and XI give the necessary general observations to be made in this regard: In the normal flame of hydrocarbons, there occur especially the bands of  $\text{CH-}$ ,  $\text{CC-}$ , and  $\text{OH-radicals}$ . Rassweiler and Withrow<sup>4</sup> had observed the following in earlier experiments: The intensity of the  $\text{CH}$  and  $\text{C}_2$  bands in the knocking zone is considerably decreased as compared with that observed in nonknocking combustion.<sup>5</sup> If knocking is suppressed

<sup>1</sup> WITHROW, L., and G.M. RASSWEILER, *Ind. Eng. Chem.*, **27**, 872 (1935); also *J. Applied Phys.*, **9**, 362 (1938).

<sup>2</sup> EGERTON and UBBELOHDE, quoted p. 539.

<sup>3</sup> EGERTON and PIDGEON, *Proc. Roy. Soc. London, A*, **142**, 26 (1933); also UBBELOHDE, quoted p. 399.

<sup>4</sup> RASSWEILER and WITHROW, *Ind. Eng.*, **23**, 769 (1931); **24**, 528 (1932).

<sup>5</sup> It would be interesting to determine whether a connection exists between this phenomenon and the often observed reduction of intensity in the primary flame with knocking combustion; cf. p. 519.

by  $\text{Pb(eth)}_4$ , the CH and CC bands are again emitted with normal intensity. The explanation originally given by Rassweiler and Withrow, that an increased use of  $\text{C}_2$  and CH—approximately according to this



is responsible for the decrease of these bands, does not seem very plausible to us. It seems improbable in the first place because the course of these reactions may always be assumed while these radicals are present at all; and secondly because these radicals are probably emitted when originated in an energy-producing reaction, which is not influenced further by a subsequent use of these same radicals. It is therefore more correct to assume that the reactions leading to the formation of the radicals is already being influenced.

As a summary of the results, we might state: Experiments all show that pre-reactions in the unburned-gas remainder cause knocking (*cf.* especially Pelletier and collaborators, quoted page 539). The exact nature of these reactions has to date not been explained with absolute certainty; even tentative interpretations require evaluation of collateral experiences, especially of the material on hydrocarbon combustion collected in the preceding chapter. The juxtaposition of results gained by other means with experiences gained in knock testing is very instructive.

**9. Knock Behavior and Chemical Constitution.<sup>1</sup> Reaction-kinetic Equations.**—It is possible to regard the problem from a different standpoint. According to the previous statements and those still to be made, any mechanism assumed as leading to knocking must contain essentially hypothetical elements, simply because only a few of the many possible reactions have been investigated. It is natural to ask whether it is possible to arrive at more than obvious conclusions by using only the most reliable data. This question will now be considered.

What can be assumed as generally reliable data?

I. That knocking is connected with a pre-reaction of the unburned mixture; this pre-reaction is responsible for the phenomena observed when it exceeds a certain critical limit.

II. That the pre-reaction in question is a chain reaction frequently with probably very long chains and with chain-branching with ramifications.

That it must be a chain reaction follows from everything that has been said in the preceding chapter concerning hydrocarbon oxidation. Independent of this, however, it may be arrived at from observations

<sup>1</sup> In connection with the fuel problem of the Otto engine, *cf.* especially also the papers by H. Bütefisch, G.B. Bonino, G. Natta, F. Neugebauer, and M. Pier read at the Convention of the German Academy of Aeronautical Research, Berlin, 1939, published in *Schriften deut. Akad. Luftfahrtforsch.*, 1939.

in engine operation: Reaction may be very much accelerated or decelerated by very small additions of certain substances. The great influence of small quantities of additions (less than 1 part per thousand of the reacting substance) always presupposes that many reaction steps of the reacting substance are affected through one reaction step of the added substance. That is imaginable only in a chain reaction where an extended sequence of reaction steps can be induced or stopped by a single step. The engine data pertinent here are: first, the effect of the antiknock substances, which can be thought of only as chain-stopping; second, the opposite effect of the proknock substances like ozone, nitrites, and certain peroxides, and, according to Egerton and collaborators, certain compounds that decompose easily with cleavage of atoms, free radicals, or compounds especially capable of reaction. That these proknock substances are effective in just as small quantities as the antiknock ones speaks most clearly for the chain character of the reactions caused or suppressed by them. Reports about compounds that are positively or negatively effective, and, according to what law, required special assumptions concerning the character of the reactions that take place. Here too, however, a few quite general statements can be arrived at if the material concerning knock behavior of different hydrocarbons and the influence on them by additions is collected and clearly arranged. Investigations concerning the knock behavior of pure hydrocarbons as well as the influence on knocking by additions have been published by Ricardo<sup>1</sup> and collaborators, Nash and Howes,<sup>2</sup> and other British investigators, also in a large number of publications of the General Motors Corporation laboratories,<sup>3</sup> and by Boyd and collaborators. Of German investigations, those by Hofmann and collaborators may be mentioned.<sup>4</sup>

The results of individual authors, together with data concerning the method used, are given in Table 112. The oldest such measurements were made by Ricardo.<sup>5</sup>

<sup>1</sup> RICARDO, H.R., "Schnellaufende Verbrennungsmotoren," Berlin, 1932. *PRE*, "Brennkraftmaschinen," translated by Dr. Ing. F. Wettstädt, Berlin, 1933.

<sup>2</sup> NASH and HOWES, "The Principles of Motor Fuel Preparation and Application," London, 1934-1935.

<sup>3</sup> CAMPBELL, J.M., W.G. LEVELL, and T.A. BOYD, *SAE J.*, **26**, 163 (1930); *Ind. Eng. Chem.*, **23**, 26, 555 (1931); **25**, 1107 (1933); **26**, 475, 1105 (1934); **27**, 593 (1935).

<sup>4</sup> HOFMANN, LANG, BERLIN, and A.W. SCHMIDT, *Brennstoff-Chem.*, **13**, 161 (1932); **14**, 103 (1933). Cf. also the papers read at the World Petroleum Conference, *World Petroleum Congress Proc.* II, 1933; especially the critical survey over mixed octane numbers by F.H. Garner, E.B. Evans, C.G. Sprake, and W.E.J. Brown, *World Petroleum Congress Proc.* II, 1933, p. 170; also the summarizing work by W.G. Lovell and J.M. Campbell, "The Science of Petroleum," Vol. IV, p. 3004, Oxford, 1938; also *Chem. Rev.*, **22**, 159 (1938).

<sup>5</sup> RICARDO, H.R., quoted p. 554.

Boyd and collaborators determined critical compression ratios for a large number of pure hydrocarbons in a single cylinder with variable compression (Table 113). Critical compression ratios were determined

TABLE 112.—CRITICAL COMPRESSION RATIOS (C.C.R.) OF PARAFFINS, OLEFINS, AND DIOLEFINS, AS WELL AS THE RAISING OF THE C.C.R. BY THE ADDITION OF LEAD TETRAETHYL (ABSOLUTE AND RELATIVE) (FROM BOYD AND ASSOCIATES)

Method (cf. the Text) Is About Equivalent to the CFR Research Method

| Olefins and diolefins <sup>1</sup>   | c.c.r. | Δ c.c.r. with the addition of 1 cm <sup>3</sup> Pb(eth) <sub>4</sub> per gal (3.81) | Δ %  | Paraffins                    | c.c.r.           | Δ c.c.r. with the addition of 1 cm <sup>3</sup> Pb(eth) <sub>4</sub> per gal (3.81) | Δ %              |
|--|--------|---|------|------------------------------|------------------|---|------------------|
| Ethylene.....  | 8.5    | —   | —    | Methane.....                 | >15              | —   | —                |
| Propylene.....   | 8.4    | —   | —    | Ethane.....                  | 14.0             | —   | —                |
| 1-Pentene.....   | 5.8    | 0.30  | 5.2  | Propane.....                 | 12.0             | —   | —                |
| 2-Pentene.....   | 7.0    | 0.50  | 7.1  | <i>n</i> -Pentane.....       | 3.8              | 0.50  | 13.1             |
|  |        |   |      | <i>n</i> -Pentane.....       | 3.8              | 0.50  |                  |
| 2-Methyl-2-butene.....   | 7.0    | 0.70  | 10.0 | Isopentane.....              | 5.7              | 0.95  | 16.7             |
| 2,3-Dimethyl butadiene.....  | 8.6    | 0.10  | 1.2  | —                            | —                | —   | —                |
| 2,4-Hexadiene.....   | 6.6    | 0.10  | 1.5  | <i>n</i> -Hexane.....        | 3.3              | 0.20  | 6.1              |
| 1,5-Hexadiene.....   | 4.8    | 0.25  | 5.2  | <i>n</i> -Hexane.....        | 3.3              | 0.20  |                  |
| 1-Hexene.....  | 4.6    | —   | —    | <i>n</i> -Hexane.....        | 3.3              | 0.20  |                  |
| 2-Hexene.....  | 5.4    | —   | —    |                              |                  |   |                  |
| 1-Heptene.....   | 3.7    | 0.25  | 6.8  | <i>n</i> -Heptane.....       | 2.8              | 0.20  | 7.1              |
| 3-Heptene.....   | 4.9    | 0.80  | 16.3 | <i>n</i> -Heptane.....       | 2.8              | 0.20  |                  |
| 3-Ethyl-2-pentene.....   | 6.6    | 0.50  | 7.6  | <i>n</i> -Heptane.....       | 2.8              | 0.20  |                  |
| 2,2-Dimethyl-4-pentene.....  | 10.0   | —   | 8.0  | 3-Ethyl pentane.....         | 3.0              | 0.20  | 5.1              |
| 2,4-Dimethyl-2-pentene.....  | 8.8    | —   | —    | 2,4-Dimethyl pentane.....    | 5.0              | 0.80  | 16.0             |
| 2-Methyl-5-hexene.....   | 4.7    | 0.25  | 5.3  | —                            | —                | —   | 7.1 <sup>2</sup> |
| 3-Methyl-5-hexene.....   | 5.0    | 0.20  | 4.0  | —                            | —                | —   |                  |
| 2,2,3-Trimethyl-3-butene.....  | 12.6   | —   | —    | 2,2,3-Trimethyl butane.....  | 13.0             | —   | —                |
| 1-Octene.....  | 3.4    | 0.15  | 4.4  | <i>n</i> -Octane.....        | 2.6 <sup>1</sup> | 0.2 <sup>1</sup>  | ~ 8 <sup>3</sup> |
| 2,2,4-Trimethyl-3-pentene.....   | 10.0   | 0.35  | 3.5  | 2,2,4-Trimethyl pentane..... | 7.7              | 2.10  | 27.3             |
| 2,2,4-Trimethyl-4-pentene.....   | 11.3   | 0.25  | 2.2  | 2,2,4-Trimethyl pentane..... | 7.7              | 2.10  |                  |
| Relative increase of the critical compression ratio by addition of 1 cm <sup>3</sup> of lead tetraethyl per gallon on the average..... |        |   | 5.9  | 2,7-Dimethyl octane.....     | 3.3              | 0.20  | 6.1              |
|  |        |   |      | 3,4-Diethyl hexane.....      | 3.9              | 0.30  | 7.7              |
|  |        |   |      | —                            | —                | —   | 10.9             |

<sup>1</sup> Diolefin in italics.

<sup>2</sup> The values of *n*-heptane for comparison.

<sup>3</sup> Estimated (from *n*-hexane and *n*-heptane).

for barely audible knocking with full load,  $n = 600$  rpm, and cooling water at boiling temperature of 100°C; mixture composition and ignition adjustment were for maximum efficiency. These conditions are approximately comparable with the CFR research method.

TABLE 113.—CRITICAL COMPRESSION RATIOS FOR ACETYLENE HYDROCARBONS (FROM BOYD AND ASSOCIATES)

| Hydrocarbon    | Critical compression ratio | Ac.c.r. with the addition of 1 cm <sup>3</sup> Pb(eth) <sub>4</sub> per gal | Δ%  |
|----------------|----------------------------|---|-----|
| Acetylene..... | 4.6                        | —   | —   |
| 1-Heptene..... | 4.9                        | 0.33—   | 6.7 |
| 3-Heptene..... | 3.4                        | 0.10  | 2.9 |
| 2-Octene.....  | 4.0                        | 0.10  | 2.5 |
|                |                            | Average.....  | 4   |

The preceding tables show a number of regularities that are to a large extent comparable with what was collected in the preceding chapter about slow oxidation of hydrocarbons. These factors deserve special emphasis:

*a.* In the series of the *n*-paraffins, knock resistance decreases with growing chain length.

*b.* This is similarly true for olefins. Since here the position of the double bonds in substances of equal C-atom numbers causes differences, it is necessary to fix the position of the double bonds for comparison. In considering olefins, for instance,<sup>1</sup> the rule stated under (*a*) becomes immediately obvious. The material is not sufficient to derive a rule for acetylene hydrocarbons. Even if in paraffins as in olefins knock resistance decreases with an increase in the number of C-atoms, this decrease does not take place at an equal rate in both. In consequence, the curves for both intersect in the vicinity of butane. If we disregard the first members of the series where olefins and acetylenes are less knock resistant than the corresponding paraffins, then it is exactly true (from approximately butane on up) of the hydrocarbons important in liquid fuels that

*c.* With equal chain length and structure, and introduction of a double or triple bond, knock resistance is generally increased (the first members excepted).

*d.* Among olefins with the straight chain,  $\alpha$  olefins seem to show least knock resistance.

*e.* It is true in paraffins as well as in olefins that, with equal size of molecule, knock resistance is increased by branching of the chain; *e.g.*, the critical compression ratio for *n*-heptane of 2.8 rises to 13 for the most symmetric heptane, 2,2,3-trimethyl butane. In this class of the branched knock-resisting paraffins belongs also 2,2,4-trimethyl pentane, which is used as the knock standard and has recently been manufactured as

<sup>1</sup> Shifting the double bond toward the middle of the molecule has a similar favorable effect on knock resistance, as does branching.

TABLE 114.—CRITICAL COMPRESSION RATIOS (c.c.r.) OF NAPHTHALENES (SATURATED) AS WELL AS ABSOLUTE AND RELATIVE INCREASING OF THE RATIO BY LEAD ADDITIONS (FROM BOYD AND ASSOCIATES, AS IN TABLE 112)

| Substance  | c.c.r. | $\Delta$ c.c.r.<br>with lead<br>additions | $\Delta\%$ |
|--|--------|---|------------|
| Cyclopentane.....  | 10.8   | 2.7                                       | 25         |
| Ethyl cyclopentane.....  | 3.9    | —   | —          |
| 1,3-Dimethyl cyclopentane.....   | 4.2    | —   | —          |
| 1,3-Methyl ethyl cyclopentane.....   | 3.6    | —   | —          |
| <i>n</i> -Amyl cyclopentane.....   | 2.8    | —   | —          |
| Cyclohexane.....   | 4.5    | 0.65                                      | 14.4       |
| Methyl cyclohexane.....  | 4.6    | 0.30                                      | 6.5        |
| 1,2-Dimethyl cyclohexane.....  | 5.1    | 0.35                                      | 6.9        |
| 1,3-Dimethyl cyclohexane.....  | 4.4    | 0.21                                      | 4.8        |
| 1,4-Dimethyl cyclohexane.....  | 4.3    | —   | —          |
| Ethyl cyclohexane.....   | 3.8    | —   | —          |
| 1,2-Methyl ethyl cyclohexane.....  | 4.3    | 0.16                                      | 3.7        |
| 1,3-Methyl ethyl cyclohexane.....  | 3.8    | 0.12                                      | 3.2        |
| 1,4-Methyl ethyl cyclohexane.....  | 3.7    | 0.13                                      | 3.5        |
| <i>n</i> -Butyl cyclohexane.....   | 3.3    | —   | —          |
| <i>s</i> -Butyl cyclohexane.....   | 3.6    | —   | —          |
| 1,2-Methyl- <i>n</i> -propyl cyclohexane.....  | 3.6    | 0.12                                      | 3.3        |
| 1,3-Methyl- <i>n</i> -propyl cyclohexane.....  | 3.4    | 0.12                                      | 3.5        |
| 1,4-Methyl- <i>n</i> -propyl cyclohexane.....  | 3.3    | 0.12                                      | 3.6        |
| 1,4-Methyl-isopropyl cyclohexane.....  | 4.0    | 0.26                                      | 6.5        |
| 1,3-Diethyl cyclohexane.....   | 3.2    | —   | —          |
| 1,4-Diethyl cyclohexane.....   | 3.3    | —   | —          |
| <i>n</i> -Amyl cyclohexane.....  | 3.1    | —   | —          |
| Iso-amyl cyclohexane.....  | 3.3    | —   | —          |
| tert-Amyl cyclohexane.....   | 4.2    | —   | —          |
| 1,2-Methyl- <i>n</i> -butyl cyclohexane.....   | 3.4    | 0.10                                      | 2.9        |
| 1,3-Methyl- <i>n</i> -butyl cyclohexane.....   | 3.3    | 0.10                                      | 3.0        |
| 1,4-methyl- <i>n</i> -butyl cyclohexane.....   | 3.2    | 0.10                                      | 3.1        |
| 1,2-Methyl- <i>n</i> -amyl cyclohexane.....  | 3.2    | 0.10                                      | 3.1        |
| Decahydronaphthalene.....  | 3.6    | 0.13                                      | 3.6        |
| Relative increasing of the c.c.r. with the addition of 1 cm <sup>3</sup> of lead tetraethyl<br>per gallon. on the average..... |        |   | 5.9        |

the most knock-resisting airplane gasoline—iso-octane with the octane number of 100.

The improvement of knock behavior by the insertion of double bonds is striking, the more so since an opposite conclusion seems natural at first from the special reactivity of the olefins, well known from organic chemistry. This behavior, however, closely follows also the experiences with hydrocarbon oxidation (*cf.* the preceding chapter). The effect of double bonds becomes even more noticeable in connected double bonds in diolefins; *cf.* Table 114.

The use of unsaturated hydrocarbons, especially those with connected double bonds, is prevented by their polymerizability, oxidizability in solution, and resin formation that interferes with engine operation. In the series of the naphthenes, *i.e.*, of the ring-shaped aliphatic combustions, the above-mentioned conformity to rule repeats itself, as can be seen from Tables 114 and 115.

TABLE 115.—CRITICAL COMPRESSION RATIOS FOR NAPHTHALENES (UNSATURATED)  
(FROM BOYD AND ASSOCIATES, *cf.* TABLE 112)

|  | c.c.r. | $\Delta$ c.c.r. | $\Delta\%$ |
|--|--------|-----------------|------------|
| Cyclopentadiene.....   | 10.9   | -0.90           | -8.3       |
| Dimethyl fulvene.....  | 9.2    | -0.13           | -1.4       |
| Indene.....  | 11.2   | -0.10           | -0.9       |
| Dicyclopentadiene.....   | 11.0   | -0.30           | -2.7       |
| Cycopentene.....   | 7.9    | 0.20            | +2.5       |
| 1,3-Cyclohexadiene.....  | 5.9    | -0.02           | -0.3       |
| Cyclohexene.....   | 4.8    | 0.20            | +4.2       |
| 1 Methyl cyclohexene.....  | 4.8    | —               | —          |
| Dipentene.....   | 5.9    | 0.25            | +4.2       |
| Relative increase of the c.c.r. with the addition of 1 cm <sup>3</sup> Pb(eth) <sub>4</sub> per gal,<br>as an average..... |        |                 | -0.3       |

TABLE 116.—CRITICAL COMPRESSION RATIOS FOR AROMATICS (FROM BOYD AND ASSOCIATES, *cf.* TABLE 112)

| Substance                    | c.c.r. | $\Delta$ c.c.r. | Substance                 | c.c.r. | $\Delta$ c.c.r. |
|------------------------------|--------|-----------------|---------------------------|--------|-----------------|
| Benzol.....                  | >15    | —               | Cymol (1,4-methyl-iso-    |        |                 |
| Toluol.....                  | 13.6   | —               | propyl benzol).....       | 11.1   | 1.0             |
| Ethyl benzol.....            | 10.5   | 2.0             | 1,3-diethyl benzol.....   | 10.8   | —               |
| <i>o</i> -Xylol.....         | 9.6    | —               | 1,4-Diethyl benzol.....   | 9.3    | —               |
| <i>m</i> -Xylol.....         | 13.6   | —               | tert-Amyl benzol.....     | 12.1   | 2.0             |
| <i>p</i> -Xylol.....         | 14.2   | —               | Phenyl acetylene.....     | 12.4   | -0.80           |
| <i>n</i> -Propyl benzol..... | 10.1   | —               | Phenyl ethylene.....      | 14.0   | —               |
| Isopropyl benzol.....        | 11.9   | —               | Benzyl acetylene.....     | 7.4    | 0.12            |
| Mesitylene.....              | 14.8   | —               | Methyl, phenyl acetylene. | 11.8   | -0.30           |
| <i>n</i> -Butyl benzol.....  | 7.7    | —               | Phenyl butadiene.....     | 9.5    | 0.00            |
| sec-Butyl benzol.....        | 10.1   | —               | Trimethyl phenylallene..  | 8.3    | -0.20           |
| tert-Butyl benzol.....       | 12.5   | —               |                           |        |                 |

Returning to our initial inquiry to consider knocking only by using the best data, the following conclusions may be drawn.<sup>1</sup> As mentioned several times, the knocking process represents the course of chain reactions. In general, the velocity of a chain reaction (*cf.* pages 258*ff.*), which parallels the knock tendency, is the greater

<sup>1</sup> For this discussion, *cf.* W. Jost and L. v. Muffling, *Z. Elektrochem.*, **45**, 93 (1939).

1. The *greater* the probability of chain-inducing processes is.
2. The *greater* the probability of chain-branching processes is.
3. The *smaller* the probability of chain-stopping processes is.

TABLE 117.—OCTANE NUMBERS FOR PARAFFINS (FROM EGLOFF,<sup>1</sup> CFR ENGINE METHOD)

| Substance                 | Octane numbers | Substance                    | Octane numbers |
|---------------------------|----------------|------------------------------|----------------|
| Methane.....              | 125+           | 2,3-Dimethyl butane.....     | 95             |
| Ethane.....               | 125+           | <i>n</i> -Hexane.....        | 0              |
| Propane.....              | 125+           |                              |                |
| Butane                    |                | Heptane                      |                |
| Isobutane.....            | 99             | 2,2-Dimethyl pentane.....    | 93             |
| <i>n</i> -Butane.....     | 91             | 2,3-Dimethyl pentane.....    | 85             |
|                           |                | 2,4-Dimethyl pentane.....    | 90             |
| Pentane                   |                | 2-Methyl hexane.....         | 64             |
| 2,2-Dimethyl propane..... | 83             | <i>n</i> -Heptane.....       | 0              |
| Isopentane.....           | 90             |                              |                |
| <i>n</i> -Pentane.....    | 64             | Octane                       |                |
| Hexane                    |                | <i>n</i> -Octane.....        | -28            |
| 2,2-Dimethyl butane.....  | 95             | 2,2,3-Trimethyl pentane..... | 101            |
|                           |                | 2,2,4-Trimethyl pentane..... | 100            |

<sup>1</sup> EGLOFF, G., *J. Inst. Petroleum Tech.* **23**, 645 (1937).TABLE 118.—OCTANE NUMBERS OF ETHERS AND MIXED OCTANE NUMBERS (FROM EGLOFF,<sup>1</sup> CFR ENGINE METHOD)

| Substance                              | Octane number | Mixed octane value in 25% mixture with 74-octane aviation gasoline + 1 cm <sup>3</sup> Pb(eth) <sub>4</sub> per gal |
|--|---------------|---|
| Di-isopropyl ether.....                | 101           | 105   |
| Methyl isopropyl ether.....            | 73            | 90  |
| Methyl-tert-butyl ether.....           | 111           | 106   |
| Methyl-tert-amyl ether.....            | 108           | 108   |
| Ethyl-isopropyl ether.....             | 75            | 87  |
| Ethyl-sec-butyl ether.....             | 63            | 73  |
| Ethyl-tert-butyl ether.....            | 115           | 114   |
| Ethyl-tert-amyl ether.....             | 112           | 106   |
| Isopropyl-tert-butyl ether.....        | 112           | 118   |
| <i>n</i> -Propyl-tert-butyl ether..... | 103           | 106   |
| Di-sec-butyl ether.....                | 95            | —   |
| sec-Butyl-tert-butyl ether.....        | 106           | 105   |
| tert-Butyl- <i>n</i> -butyl ether..... | 81            | 92  |
| tert-butyl- <i>n</i> -amyl ether.....  | 63            | 80  |

<sup>1</sup> EGLOFF, G., *J. Inst. Petroleum Tech.*, **23**, 645 (1937).Cf. also BANKS, F.R., Some Problems of Modern High-duty Aero Engines and Their Fuels, *J. Inst. Petroleum Tech.*, **23**, 63 (1937).

Ketones are likewise very knock-resistant and show a high lead sensitivity.



The above-mentioned data concerning knock behavior of different hydrocarbons, as well as behavior in slow oxidation, are compatible from the standpoint of chain-process theory with the apparently opposite data of organic chemistry, namely, that the paraffins are least and the olefins most reactive, in contrast to knocking, if the following assumptions are made:

TABLE 119.—OCTANE NUMBERS OF ALCOHOLS (FROM EGLOFF,<sup>1</sup> CFR ENGINE METHOD)

| Methanol | Ethanol | <i>n</i> -Butanol | Iso-butanol | sec-Butanol | tert-Butanol                                  | Amyl | tert-Amyl                                       |
|----------|---------|-------------------|-------------|-------------|---|------|---|
| 98       | 99.5    | 87.5              | 87.5        | —           | 100 + (isooctane + 3 lead tetraethyl per gal) | 77.5 | 100 + (isooctane + 0.2 lead tetraethyl per gal) |

<sup>1</sup> EGLOFF, G. J. *Inst. Petroleum Tech.*, **23**, 645 (1937).

Cf. also BANKS, F.R., Some Problems of Modern High-duty Aero Engines and Their Fuels, *J. Inst. Petroleum Tech.* **23**, 63 (1937).

In mixture with 70-octane gasoline, the alcohols also show a good lead sensitivity.

I. The great oxidizability of paraffins in knocking is caused in spite of small reactivity of the individual molecule (or small probability of the introduction of a chain induction) by the fact that the chain stopping is very improbable and, consequently, long reaction chains occur.

II. For the relative knock resistance of the olefins (with their probably significant reactivity of the individual molecule and thus considerable probability of chain induction), it must be assumed that the chain-stopping reactions are very probable and that thus the reaction chains are relatively short. It can be easily imagined that a chain-continuing compound reacts with the double bond of the initial molecule.

If the assumptions in I and II are accepted as working hypotheses, a number of consequences that can be verified in experience result. The question of what can be said about the effect of additions and about the behavior of mixtures arises. For the sake of brevity, fuels are designated as being class I and II if under ideal conditions they fit the statements made under I and II. For instance, paraffins and naphthenes would belong to group I—with probability of chain stoppage; unsaturated fuels of all kinds (though aromatic compounds cannot be included here without qualification and would have to be treated separately) would belong to class II—with great probability of chain stoppage.

If, furthermore, an antiknock compound is characterized as a compound with chain-stopping properties [it is not implied by this that the compound as such has these properties, but perhaps only its products of decomposition like Pb or lead oxides in the case of Pb(eth)<sub>4</sub>, iron oxide

or iron in the case of  $\text{Fe}(\text{CO})_5$ ], certainly the addition of such a compound would have to be the more effective the less often chain stoppage takes place without it. That is, in a paraffin or saturated naphthene, a stronger antiknock effect is to be expected than in the corresponding unsaturated compound. Extensive material concerning the effect of additions is available only for  $\text{Pb}(\text{eth})_4$ , again mainly in the work of Boyd and collaborators; it fulfills these expectations. In the above tables, the increases in the critical compression ratios with the addition of  $1 \text{ cm}^3$  of tetraethyl lead to the American gallon ( $\sim 3.8$  liters) are added.

A 5.9 per cent for olefin and 4 per cent for acetylene is obtained as the average relative increase of the critical compression ratio in Table 112, but 10.9 per cent is obtained for the paraffins. The difference is striking in the direction where it was expected; it shows also in the individual fuels with only two exceptions,<sup>1</sup> which, in view of the constitutive influences that may always enter, should surprise no one. The same regularity is, on the average, valid also for the absolute increase of the compression ratio, although here more pronounced individual deviations have been observed. It will be shown later that the relative increase should be regarded as the more significant measure.

The same is true for the naphthenes (Table 114). Here the relative increase of the critical compression ratio by lead addition amounts, on the average, to 5.9 per cent (this happens to be the same as with isomeric olefins) in the case of the saturated ones. For the single and multiple unsaturated naphthenes, on the average, a deterioration of knock behavior results,  $\Delta \text{c.c.r.}$  becomes on the average  $-0.3$  per cent, but  $\Delta$  becomes negative only with the multiple unsaturated ones (Table 115). The difference between saturated and unsaturated compounds is on the average the same as in paraffins.

Aromatic compounds (Table 116) show no uniform behavior. This is not surprising, since the nature of the substitutes is essentially involved in the character of the compound. Thus, in the case of aromatics with aliphatic side chains, the aliphatic character will show up, especially when the side chains are branched. Their lead sensitivity is comparatively high; but conversely, in the case of unsaturated substitutes, lead sensitivity becomes low and effect often shows a negative sign.

The observed effect of lead tetraethyl verifies essentially the expectations described above on the basis of chain reactions. In this connection, some individual peculiarities and more general relations appear, which will now be discussed in part.

<sup>1</sup> It is remarkable that these exceptions are  $\beta$  and  $\gamma$  olefin; they are more knock-resisting than  $\alpha$  olefin and apparently resemble in their character the branched paraffins.

a. In unsaturated compounds, lead sensitivity increases with increasing branching and also when the double bond moves toward the center of the molecule.

b. In acetylene hydrocarbons, in contrast, the improvement in knock behavior through addition of lead tetraethyl becomes smaller the farther the triple bond moves toward the center of the molecule.

c. In aromatic compounds, lead sensitivity increases the more the side chain corresponds to knock-resisting paraffins.

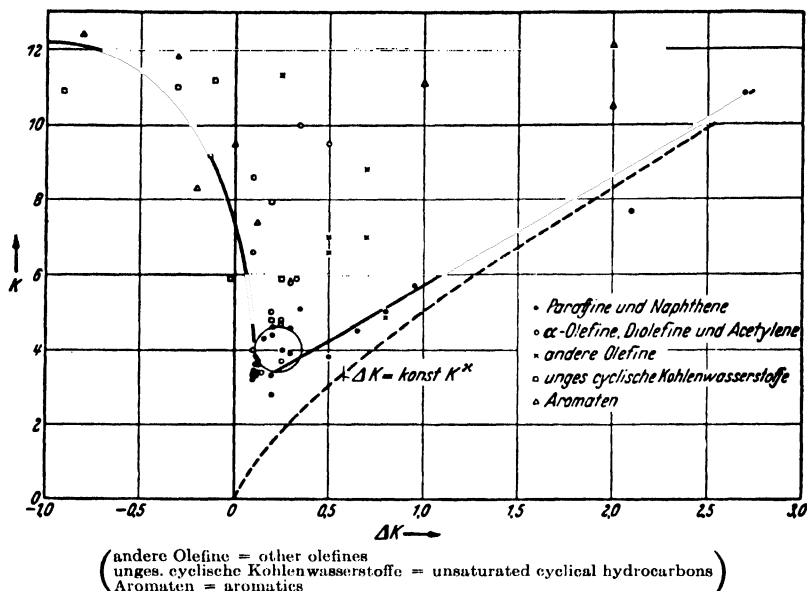


FIG. 262.—Critical compression ratio  $K$ , as well as increase of the critical compression ratio with addition of 1 cm<sup>3</sup> of tetraethyl lead per gallon  $\Delta K$  for various hydrocarbon groups. (From Lovell, Campbell, and Boyd, p. 545.)

Figure 262, after Boyd and collaborators, clearly shows the different behavior of the different groups of hydrocarbons.

Since tetraethyl lead is less effective the more chains are stopped at their inception, additional tetraethyl lead would have less effect if by a previous addition improvement in knock quality had already been caused. This is also verified by the experiments of Hebl and Rendel.<sup>1</sup>

In general, then, no linear relation exists between lead addition and improvement in knock resistance (except for very small additions). The experiences with the effect of lead in various concentrations and the difference of its effect with saturated and unsaturated hydrocarbons can be thus tentatively summarized: Unsaturated hydrocarbons appear, on the average, more knock-resisting than the saturated ones (paraffins

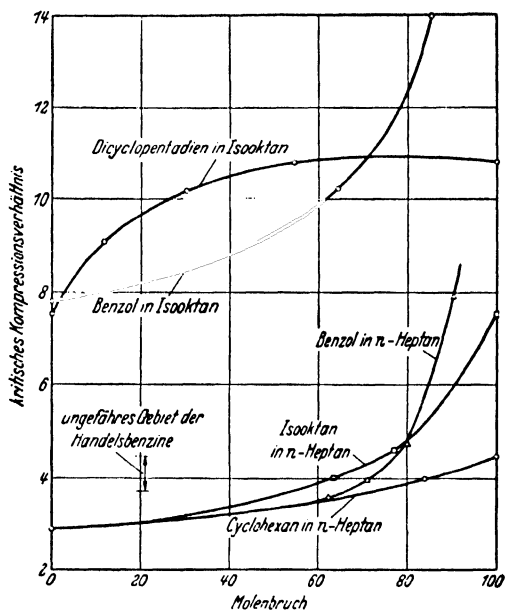
<sup>1</sup> HEBL, L.E., and T.B. RENDEL, *J. Inst. Petroleum Tech.*, **17**, 187 (1931).

or naphthenes) because the multiple bond has a chain-stopping effect, like an antiknock substance; *i.e.*, roughly speaking, unsaturated hydrocarbons behave like saturated ones to which antiknock substances have been added. In either case, additional antiknock substances will be less effective than with saturated hydrocarbons that have had no antiknock additions.

The statements that a fuel is knock-resisting because few chains run their course in it and that it is knock-resisting because in it many chains are stopped permit conclusions concerning the probable behavior of these substances in mixtures. If a more knock-resisting fuel is added to a less resistant one like *n*-heptane, the effect of the stronger will be (1) a dilution of the less resisting fuel, but (2) under certain conditions also an influence on the course of the combustion. The first effect might be calculated according to the rule of mixtures, presupposing a rational measuring unit, for which the octane number does not come into consideration. The second influence may cause an improvement or a deterioration of the resulting knock behavior. If the added fuel possesses a strong chain-breaking effect, the mixture will be expected to have higher knock resistance than has been calculated from the rule of mixtures. The octane number that would have to be ascribed to the added fuel, in order to have the empirical octane number of the mixture agree with the computed one, is called "mixture octane number." If the representations concerning different groups of fuels developed earlier are correct, those of class I (with small probability of chain stoppage and relatively high lead sensitivity) with equal knock resistance in pure form would have to have, in general, lower mixture octane numbers than those of class II (with great probability of chain stoppage and small lead sensitivity). This is again a conclusion that is corroborated to a large extent by experience. Figure 263, according to Lovell, Campbell, and Boyd,<sup>1</sup> shows primarily critical compression ratios (determined according to the same method given on page 555, *i.e.*, approximately equivalent to the CFR research method) for a number of mixtures. The first component is always either *n*-heptane or iso-octane; for the second component, cyclohexane, iso-octane, benzene, and, in one case as a typical multiple unsaturated compound, dicyclopentadiene were selected. Although, in all other cases, small additions of the more knock-resisting compounds effected only a comparatively small improvement of the characteristics of the mixture, the influence of the unsaturated dicyclopentadiene in small concentrations is remarkably great, as is to be expected according to previous discussion. On the behavior of the iso-octane-*n*-heptane mixtures, *cf.* also the conditions in slow oxidation (Chap. XI, pages 459ff.). Figure 263, as also Fig. 261, which represents a different method,

<sup>1</sup> LOVELL, CAMPBELL, and BOYD, *Ind. Eng. Chem.*, **26**, 1105 (1934).

shows that the octane scale is a very uneven yardstick for measuring knock resistance. Change by one unit represents a much smaller change of the critical compression ratio at low octane numbers than at high octane numbers. This lack of uniformity becomes less noticeable when the final temperatures reached in compression are considered instead of compression ratios; for the higher compression ratio change by one unit means a smaller rise in temperature than with lower compression ratios; but lack of uniformity remains nevertheless.



(kritisches Kompressionsverhältnis = critical compression ratio  
ungefähres Gebiet der Handelsbenzine = approximate range of commercial gasolines)  
Molenbruch = mol fraction

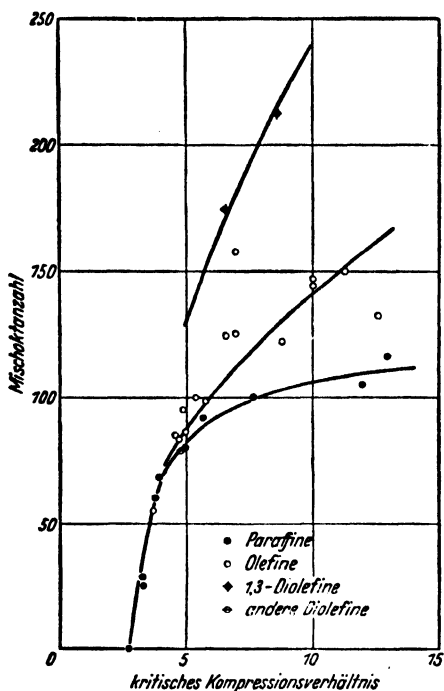
FIG. 263.—Critical compression ratios of various mixtures (research method); the mol-fraction of the more knock-resistant components in the mixture is plotted as the abscissa. The particularly strong effect of small additions of dicyclopentadien is remarkable. (From Lovell, Campbell, and Boyd<sup>1</sup>.)

Lovell, Campbell, and Boyd (page 554) investigated a large number of fuels in mixtures for their behavior. Their results were expressed, not in octane numbers, but in "aniline equivalents." The fuel was in each case investigated in a diluted mixture in a reference gasoline of 55-octane rating. An aniline equivalent of the fuel is that number of  $\frac{1}{100}$  gram-mol of aniline which per liter of reference gasoline effects the same change in knock value as one mol of the fuel per liter of reference gasoline. Since deterioration of knock behavior also occurs, the negative aniline equivalent for this case is defined as the corresponding aniline quantity that makes the mixture in its knock behavior again equivalent

<sup>1</sup> LOVELL, CAMPBELL, and BOYD, *Ind. Eng. Chem.*, **26**, 1105 (1934).

to the reference fuel. In itself, it is possible empirically to compute mixture octane numbers (these numbers depend, of course, on the reference fuel).

Since only relative values are of importance, a less arbitrary comparison is obtained by the direct use of the aniline equivalents. These (Fig. 264) show markedly the following behavior: With equal knock resistance (equal critical compression ratio), it is, on the average, true



(Mischoktanzahl = mixed octane number  
andere Diolefine = other diolefins  
kritisches Kompressionsverhältnis = critical compression ratio)

FIG. 264.—Aniline equivalents (as measure of the mixed octane number) plotted against the critical compression ratio for various hydrocarbon groups. (From experiments by Bodý and associates.)

for aniline equivalents that they increase greatly in the order of paraffins (or naphthene), olefin (unsaturated naphthene), and diolefin (also ring-formed). That is again exactly what was to be expected according to the preceding considerations. Furthermore it follows, of course, that, in the same order in which with equal knock resistance in pure form the mixture octane number increases, the lead sensitivity must decrease;<sup>1</sup> for the higher the mixture octane number the stronger is the chain-stopping property of the substance itself, and the less will its behavior

<sup>1</sup> Cf. in this connection JOST and v. MÜFFLING, quoted p. 558.

be influenced by chain-stopping additions. It is therefore perhaps not surprising if the known chain-inducing influence of tetraethyl lead<sup>1</sup> here makes itself felt besides its chain-stopping effect and influences knock behavior adversely.

An attempt can be made to formulate the different influences quantitatively from the standpoint of the chain-reaction velocity.<sup>2</sup> Thus expressions are obtained that are valid for the average behavior of a group of substances (because the comprehension of all individual characteristics would require an unwarranted introduction of a large number of available constants) and that are true, of course, only to that degree of approximation at which the simplified formal data of the chain theory are correct.<sup>3</sup> The expressions obtained permit a satisfactory description (1) of the different influenceability of knock behavior within a series by addition of  $\text{Pb(eth)}_4$ ; especially is it possible to obtain rather easily a limit law for the observed behavior of the paraffins and naphthenes (cf. Fig. 262, dash curve); (2) of the relative efficiency of variously large quantities of lead; and (3) of the possibility of a varying influence (which may differ even in algebraic sign) of  $\text{Pb(eth)}_4$  on the fuels of different groups.

For the comparison of the variation of the knock behavior through lead addition in various knock-resisting substances, the following qualitative consideration is called for: If the lead addition effects a restriction of the reaction and if, in consequence, the compression ratio can be increased until the beginning of knocking by a certain amount above what was determining without lead addition, the restriction of the reaction has been compensated for by a rise in temperature (in consequence of greater compression and, to a lesser extent, also by a rise in pressure). Regarding substances in which equal quantities of lead cause the same relative restriction—something probably to be expected in homologous series—the increase in compression ratio necessary for compensation of this restriction would have to be the greater, the greater this (compression ratio) originally is; for the greater the compression ratio, the smaller is the temperature rise per unit that a further increase of the same causes. This can easily be calculated. The quantitative completion of this consideration<sup>4</sup> leads, within certain such hypothetical groups of substances,<sup>5</sup> to the relationship between critical compression ratio  $\epsilon$  as well as its increase  $\Delta\epsilon$  through lead addition

<sup>1</sup> Lead tetraethyl decomposes under formation of free radicals which, for instance, can induce the decomposition of hydrocarbons.

<sup>2</sup> Jost, W., and L. v. MÜFFLING, quoted p. 558. Jost, W., L. v. MÜFFLING, and ROHRMANN, quoted p. 488.

<sup>3</sup> Jost, W., and L. v. MÜFFLING, *Z. physik. Chem., Sec. A*, **183**, 43 (1938).

<sup>4</sup> Cf. Jost, cited pp. 488, 558.

<sup>5</sup> Only those materials are comparable which have approximately the same apparent activation energy of combustion.

$$\Delta\epsilon \sim \text{const } \epsilon^*$$

in which the constant is calculable from reaction-kinetic data. As a limit law, this relationship seems to be well fulfilled, *e.g.*, in paraffins and naphthenes (Fig. 262). It is, as a matter of principle, possible to comprehend approximately through this formal the behavior of other groups of substances and to refine it so that it will account for individual characteristics, *e.g.*, include also the deterioration through lead addition of the knock behavior of multiple, unsaturated compounds. For this we must refer to the original.

**10. Antiknock Substances.**<sup>1</sup>—Although thousands of compounds have been investigated for their antiknock qualities, lead tetraethyl, discovered some 20 years ago by Midgley, is the most effective and is still largely used today. Iron carbonyl, manufactured by I.C. (Farben) is, to be sure, less effective than tetraethyl lead (with reference to mols), but its effectiveness is of the same order of magnitude. For practical purposes, antiknock effectiveness is not the only consideration, but also products like lead oxide or iron oxide that will interfere with operation should not remain in the engine. That is why tetraethyl lead is used in a mixture with ethylene bromide: the lead bromide that forms is volatile and escapes together with exhaust gases. The problems connected with this lie outside the scope of this book, however.

As follows clearly from the facts given in this and the preceding chapter, antiknock substances are such compounds as interfere with the chain reaction of the hydrocarbon oxidation in the gas phase.<sup>2</sup> In this,

TABLE 120.—RELATIVE ANTIKNOCK EFFECT (ANILINE = 1) (FROM CALINGAERT)

|   |       |
|---|-------|
| Benzol.....                               | 0.085 |
| Iso-octane (2,2,4-trimethyl pentane)..... | 0.085 |
| Ethanol.....                              | 0.104 |
| Xylol.....                                | 0.142 |
| Aniline.....                              | 1.00  |
| Ethyl iodide.....                         | 1.09  |
| Titanetetrachloride.....                  | 3.2   |
| Tin tetraethyl.....                       | 4.0   |
| Diethyl selenide.....                     | 6.9   |
| Diethyl telluride.....                    | 26.6  |
| Nickel carbonyl.....                      | 35    |
| Iron carbonyl.....                        | 50    |
| Lead tetraethyl.....                      | 118   |

<sup>1</sup> Cf. in this connection the contribution by G. Calingaert, "The Science of Petroleum," Vol. IV, pp. 3024ff.; also K.C. Bailey, "The Retardation of Chemical Reactions," Arnold, London, 1937. Bailey gives a detailed discussion of the observations on antiknock substances, and various theories, all of which must be regarded as out of date insofar as they do not describe the effect of the antiknock substances as blocking in the chain reaction.

<sup>2</sup> EGERTON, A.C., *Nature*, **119**, 427 (1927); **121**, 10 (1928). TAYLOR, H.S., *Nature*, **119**, 746 (1927).



tetraethyl, for instance, is effective only when it has decomposed (*cf.* page 547). There is no contradiction to the interpretation offered here in the fact that other substances have at room temperature a much greater effect in slowing oxidation than the effective antiknock compounds.<sup>1</sup> This means only that the oxidation slowing effectiveness of a substance can depend greatly on the experimental condition, *e.g.*, temperature.

Accordingly, all compounds that impede slow oxidation of hydrocarbons in the gas phase are practically more or less antiknock substances. Besides a number of metallic organic compounds, nitrogen-containing organic compounds especially belong in this class. Their effectiveness depends considerably on their structure. Some compounds that have an unusually high mixture octane number, like some olefins, can be counted among antiknock substances; that is largely a matter of terminology.

For the relative effectiveness of various substances (expressed by the reciprocal number of mols that cause the same antiknock effectiveness as one mol of aniline), the above survey is reproduced (according to Calingaert, quoted page 567; mainly according to Lovell, Campbell, and Boyd; also Midgley and Boyd).

Of the aromatic amines, the ones like aniline (= 1) which have at least one H-atom with nitrogen, are of comparable effectiveness. Toluidine (1.22), *m*-xylydine (1.4), and diphenyl amine, for example, are somewhat more effective than aniline. Less effective, on the other hand, are, for example, dimethyl aniline (0.21), triphenyl amine (0.09), as well as aliphatic amines like diethyl amine (0.495). Ammonia even has a slightly proknock effect. Lately aminocymol<sup>2</sup> has been described as a suitable antiknock compound of effectiveness equal to that of aniline. The fact that one H-atom must be located in the amino compound with the nitrogen might point out that the antiknock effectiveness is connected with an attack on the nitrogen, oxidizing or reducing it. It might be suggested that the greater effectiveness of metallic organic compounds, compared with amino compounds, comes from the fact that these are destroyed in the act of chain-breaking, whereas the metals can continuously interfere in the course of the reaction through multiple oxidation and reduction (probably not to metal; Egerton points out that the effective metals may all occur in two stages of oxidation).

An opposite effect from the antiknock substances is produced by the previously mentioned "knock stimulators" (page 543) like organic

<sup>1</sup> ST. LEWIS J., *J. Chem. Soc.*, 1930, p. 2241; *cf.* BAILEY, quoted p. 567.

<sup>2</sup> ERSHOV and FEDOTOVA, *J. Applied Chem. USSR*, 10, 869 (1937). "Petroleum Technology in 1937," edited by F.H. Garner, p. 229, The Institute of Petroleum, London, 1938.

peroxides, nitrites, and ozone.<sup>1</sup> The existence of these substances, which can induce chains and knocking in as small quantities as are needed of antiknock substances to discontinue chains and suppress knocking, supports the theory here developed. Doubts as to its correctness no longer exist.

The influence by antiknock substances on ignition behavior has repeatedly been encountered (*cf.* chiefly page 443). The raising of the ignition points by tetraethyl lead varies greatly according to the fuel under investigation and the condition of experimentation. Since in all but Tizard and Pye's methods the wall exerted a more or less pronounced influence on the results, the observation in the presence of  $\text{Pb(eth)}_4$  and other substances will not be independent of it. It must also be considered that these additions change the condition of the wall considerably.<sup>2</sup> The results of all such experiments are therefore applied only conditionally to engine operation. A raising of the ignition points by from a few to about 200°C by tetraethyl lead is, however, generally observable.

For such experiments in ignition testers—which, after what has been said, should be evaluated with caution—see Helmore.<sup>3</sup> Besides observations showing a raising of ignition temperature under these conditions, there are also a few that show a slight lowering. This is not surprising in view of the lack of knowledge of the effective factors.

**11. Conclusions.**<sup>4</sup>—After the experiments discussed, we should like to assume a reaction proceeding in homogeneous phase in the unburned mixture, without decisive collaboration of gas vibrations<sup>5</sup> or heterogeneous reactions (*e.g.*, on or in droplets<sup>6</sup>). Likewise, according to the data discussed, we believe that a temperature course of hydrocarbon oxidation, like that of Townend and collaborators,<sup>7</sup> is not normally to be expected under engine conditions.<sup>7</sup> Nevertheless, in special cases, a coeffectiveness of such factors cannot from the outset be excluded, and their influence in the interpretation of possible anomalies will have to be considered. We shall discuss the effect of droplets in the next chapter.

<sup>1</sup> BROOKS, D.B., *J. Inst. Petroleum Tech.*, **19**, 835 (1933).

<sup>2</sup> PIDGEON, L.M., and A.C. EGERTON, *J. Chem. Soc.*, 1932, pp. 661, 676. ST. LEWIS, J., *J. Chem. Soc.*, 1930, p. 2241.

<sup>3</sup> HELMORE, W., "The Science of Petroleum," Vol. IV, pp. 2970ff., 1938.

<sup>4</sup> In connection with combustion in engines, besides the references given in the text and in the bibliographical index, we should like to point out a paper by Banks, *J. Inst. Petroleum Tech.*, **23**, 63 (1937).

<sup>5</sup> *Cf.* pp. 512ff., 522ff.

<sup>6</sup> *Cf.* especially CALLENDAR, H.L., quoted p. 544. KING and G. MOLE, *J. Inst. Petroleum Tech.*, **21**, 838, 845, 853, (1935). Concerning the influence of lubricating oil on knocking, *cf.* King and H. Moss, *Engineering*, July 11 and 25, 1930; Jan. 2, 1931. KING, *Engineering*, Aug. 25, 1933.

<sup>7</sup> *Cf.* pp. 476ff.

No direct experiments seem to have been made to ascertain whether knocking is increased by droplets and the like. Those by King refer to auto-ignition under atmospheric pressure. With regard to shock waves, the tests of Rothrock and Spencer (quoted page 516) yielded negative results. Only indirect arguments are given, *e.g.*, by Dumanois,<sup>1</sup> that knocking does not occur if the combustion chamber is given such shape that a series of sudden enlargements of the cross section takes place in the path of the flame. Such an arrangement would counteract the occurrence of shock waves and the beginning of a true detonation; for this reason, Dumanois would like to identify knocking with such an arrangement. The special shape of the combustion chamber, however, simultaneously influences the course of the flame, turbulence, and—indirectly—cooling, so that it is not absolutely certain whether suppression of a shock wave was the decisive factor.

The fact that the temperature course, as Townend and collaborators observed it, can play a role even under engine conditions, is verified by the older experiments of Dumanois.<sup>2</sup> Proceeding from the fact that peroxides once formed begin to decompose in the vicinity of 300°C, he expected that raising of the engine temperature would cause a disappearance of knocking following a temporary increase because the peroxides responsible will have previously decomposed. Actually his experiments confirmed his expectations, but the engine under these conditions kept operating even without ignition. The interpretation that Serruys<sup>3</sup> gave to these experiments is therefore probably the correct one: Under these conditions, premature ignitions occur, and therefore the presuppositions of knocking are not any longer present. Lewis and v. Elbe<sup>4</sup> tried to make the ignition behavior, as observed by Townend, responsible for certain experiences in engine operation. Systematic experiments on knocking with automobile engines actually in operation<sup>5</sup> resulted in quite complicated relationships. Since in practical operation, however, a number of factors are changed simultaneously, it is not necessary to assume that the complications represent a characteristic of the fuel. It seems to us that the decisive point—the difficulty of a separation of fuel factors from engine factors—imposes, for the time being, utmost caution in judging this situation.

<sup>1</sup> Cf. the comprehensive treatment in "The Science of Petroleum," Vol. IV, p. 3054.

<sup>2</sup> Cf. p. 569, footnote 4.

DUMANOIS, P., *Ann. Office nat. des combust. liquides*, **9**, 141 (1934); *Compt. rend.*, **197**, 393 (1933).

<sup>3</sup> SERRUYS, M., *Compt. rend.*, **197**, 224 (1933); cf. DUMANOIS, "The Science of Petroleum."

<sup>4</sup> LEWIS, B., and G. v. ELBE, *Chem. Rev.*, **22**, 155 (1938).

<sup>5</sup> BEST, H.W., *Chem. Rev.*, **22**, 143 (1938).

## CHAPTER XIII

### COMBUSTION IN THE DIESEL ENGINE

The working process of the Diesel engine differs from that of the Otto engine only in the fact that the suction air is compressed by the piston and that the fuel is then injected into the hot, compressed air, where it ignites without a spark.

The problem of combustion in the Diesel engine is essentially different in kind from that of the Otto engine. The important thing in the Diesel engine is first, that ignition takes place at all; second, that further combustion proceeds with suitable velocity. The difficulties that can result in operation are first, as in the Otto engine, that ignition and pressure rise take place too late with subsequent loss of efficiency. As in the Otto engine this disadvantage can be largely overcome by means of advancing the ignition, so in the Diesel engine it can be largely overcome by advancing the injection. Actually, jet injection is begun at least about  $10^{\circ}$  to  $20^{\circ}$  of crank angle before upper dead center. For the following reason, however, not everything is taken care of in a longer ignition delay by the advance of the injection corresponding to the ignition delay: During ignition delay, a further quantity of fuel is injected into the combustion chamber; the longer the ignition delay, the greater is the fuel quantity found in the cylinder at the time of ignition. The more fuel present, however, the steeper the pressure rise becomes. Once actual combustion starts, the sudden combustion of too great a quantity of fuel can lead to knocking of the Diesel engine and must therefore be avoided. Knocking in Diesel engines, therefore, has a cause opposite to that of knocking in Otto engines. In the Otto engine, the cause of knocking is too great an ignitibility of the adiabatically compressed mixture; in the Diesel engine, it is too great a delay in ignition, caused by the slow ignitibility of the fuel. Accordingly, the requirements of the fuel in the two cases are very different: Normal paraffins of low octane number are badly suited for operation of the Otto engine, but they are very good for Diesel engines. The opposite is true of knock-resisting aromatic fuels. Coal-tar oils can be burned in Diesel engines only with the aid of special devices.<sup>1</sup>

As in combating knocking in the Otto engine, for the improvement of ignition in the Diesel engine two considerations enter—the influence on the part of the construction, and the influence on the part of the fuel.

<sup>1</sup> Cf., e.g., ZINNER, K., *Z. Ver. deut. Ing.*, **79**, 1319 (1935).

**1. The Working Process of the Diesel Engine.**—For the reader less familiar with engine conditions, a few observations are here presented. The constant-pressure process may be chosen (Fig. 265) as the ideal process<sup>1</sup> on which a comparison with the actually obtained efficiency is based in contrast to the constant-volume process in the Otto engine, where heat was imagined as added in and rejected under constant volume. That means the following: Assuming that at 1, Fig. 265, the suction air at volume  $v_1$  is in the cylinder; through compression in

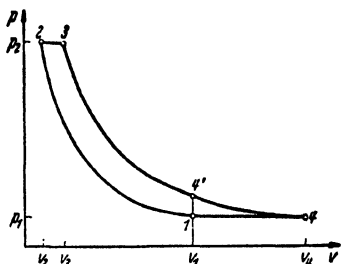


FIG. 265.—Ideal process of the equal-volume method.

ratio  $\epsilon$  to the volume  $v_2$ , pressure rises from  $p_1$  to  $p_2$  together with temperature. At the moment of maximum compression, fuel begins to be injected; for the ideal process, it is assumed to burn instantaneously. The fuel supply is regulated so that the pressure remains constant until volume  $v_3$  is reached; *i.e.*, in the case of the ideal process with air, the expansion from  $2(T_2)$  to  $3(T_3)$ , taking place at constant pressure, the heat quantity  $Q_1 = c_p(T_3 - T_2)$  is added; from 3 to 4, the gas expands adiabatically with work to 4; then the heat quantity  $Q_2 = c_p(T_4 - T_1)$  is withdrawn from the gas at constant pressure, and this brings it back to its initial stage. The efficiency is then (*cf.* the corresponding observations in Chap. XII, page 503)

$$\eta = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{T_4 - T_1}{T_3 - T_2} \quad (1)$$

Since the temperatures 1 and 2, also 3 and 4 are linked by an adiabatic,

$$\frac{T_2}{T_1} = \frac{T_3}{T_4} = \epsilon^{\kappa-1} \quad (2)$$

consequently also

$$\frac{T_3 - T_2}{T_4 - T_1} = \epsilon^{\kappa-1} \quad (3)$$

becomes this

$$\eta = 1 - \frac{1}{\epsilon^{\kappa-1}} \quad (4)$$

which is the same value as for the constant-volume process. In reality, however, the expansion takes place not to  $v_4$  but to the initial volume  $v_1$ , *i.e.*, to the point 4'. The output is therefore smaller than computed by the area 4'-4-1, the value of which can, of course be given (*cf.* footnote 1

<sup>1</sup> *Cf.* PRE, D.R., "Brennkraftmaschinen," Julius Springer, Berlin, 1932. Müller-Pouillet, "Lehrbuch der Physik," Vol. III, 1.

page 572). In actual operation, combustion takes place not under constant pressure but under conditions that lie between the constant-volume and the constant-pressure cases. Figure 266 shows the ideal process on which it is based. A part of the heat is assumed under constant volume; pressure rise from  $p_2$  to  $p_3$ ; the remaining part under constant pressure; volume expansion from  $v_3$  to  $v'_3$ ; if  $\alpha = p_3/p_2$  and  $\beta = v'_3/v_3$  are given, then the ideal efficiency can be given for this process too. It is found to be (*cf.* the quoted material)

$$\eta = 1 - \left(\frac{1}{\epsilon}\right)^{\kappa-1} \sigma \quad (5)$$

with

$$\sigma = \frac{\alpha\beta^{\kappa-1}}{\alpha - 1 - \kappa\alpha(\beta - 1)}$$

Details are of no interest here; it is essential only that, even in the Diesel engine, except for a correction factor, which means a decrease of efficiency, the expression  $1 - (1/\epsilon)^{\kappa-1}$  is the determining factor for the working efficiency. The useful effect would therefore increase if combustion took place instantaneously. That is not attainable, however, first because of finite ignition and combustion velocities, and second because of the high peak pressures thus far not technically obtainable. It is indeed the advantage of the Diesel process that, since danger of auto-ignition and knocking are not present as in the carburetor engine (on knocking in Diesel engines, see the footnote below), compression ratios can be and have to be much higher if auto-ignition of the injected fuel is to be assured. Accordingly, compression ratios of  $\sim 1:18$  occur in Diesel engines.

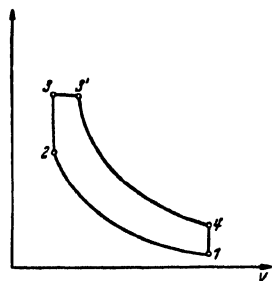


FIG. 266.—Ideal process of the volume-pressure method.

**2. General Considerations Concerning the Combustion Process in Diesel Engines, Jet Injection, Evaporation, and Ignition.**<sup>1</sup>—Figure 267 shows I, the ideal, and II, the actual pressure variations, in combustion in Diesel engines. The symmetrical lower curve would correspond to the pressure variation without fuel injection and without combustion. The ideal curve, I, would be obtained if ignition were to start immediately at the moment of injection and if the remaining fuel would burn on injec-

<sup>1</sup> Cf. RICARDO, cited p. 554. BOERLAGE and BROEZE, *Ver. deut. Ing. Forsch.*, 1934, p. 366. *J. Inst. Petroleum Tech.*, **21**, 40 (1935). "The Science of Petroleum," Vol. IV, p. 2894; *Chem. Rev.*, **22**, 61 (1938).

tion. The actual process, II, differs from this in that ignition takes place only after a certain delay period (1, Fig. 267); then the already injected fuel burns within a very short time, 2, and, as section 3 joins, combustion is essentially dictated by injection speed. Even after termination of injection, 4, an after-burning can still take place, namely, if the mixture formation was irregular or over-rich or if a part of the charge or of the injected fuel had been considerably cooled.

Figure 268, according to Zinner,<sup>1</sup> shows how much, even after ignition has started, combustion can lag behind injection, mainly on account of imperfect mixture formation.

A high degree of efficiency requires combustion as much as possible

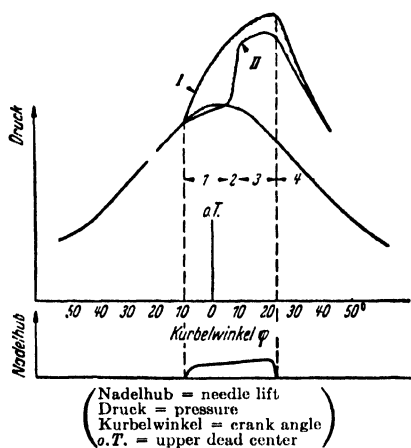


FIG. 267.—Ideal, I, and actual pressure variation, II, in Diesel-engine combustion. Beginning of injection assumed at 10° crank angle before upper dead center. 1, ignition delay. 2, complete ignition and combustion. 3, range of directed combustion. 4, after-burning. (From Boerlage and Broeze.)

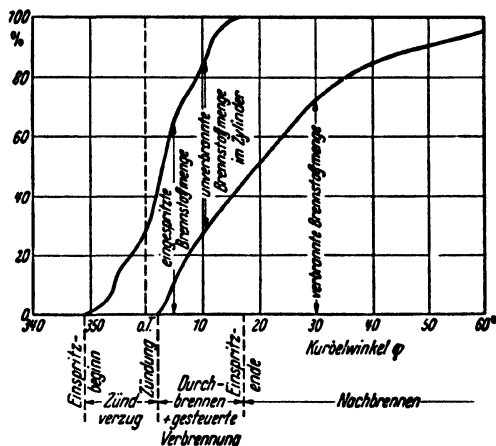
at upper dead center; but in this, on account of operational conditions, too sudden a compression rise and too high an absolute compression should be avoided. Apparently, favorable combustion in Diesel engines depends on more than only the characteristics of the fuel, for a complete combustion demands primarily a perfect mixture of the fuel with air, which, in contrast to the Otto engine, is not present from the start in the Diesel engine. This necessitates the best obtainable atomization of the injected fuel, but this alone does not suffice. The atomized fuel must also be distributed as evenly as possible through air, which is not possible without the

action of gas currents. Boerlage speaks of macromixture (distribution through air) and micromixture (fine atomization and evaporation of the fuel). These problems of the injection process, the turbulence of the air in the combustion chamber, etc., have been under careful investigation; especially the injection has been investigated by means of spark photographs (e.g., in Nägel's Institute<sup>2</sup>), but these are outside the scope of this volume. Even if an oxidation of fuels can take place as soon as in the liquid phase, the rapid oxidation that is necessary for

<sup>1</sup> ZINNER, K., *Z. Ver. deut. Ing.*, **82**, 9 (1938).

<sup>2</sup> HOLFELDER, B.O., *Ver. deut. Ing. Forsch.*, 1935, p. 374. *Z. Ver. deut. Ing.*, **80**, 193 (1936). A. Nägel, paper read at the convention of the German Academy of Aeronautical Research, Berlin, 1939; published in *Schriften deut. Akad. Luftfahrtforsch.*

combustion in the Diesel engine<sup>1</sup> can take place only in the evaporated fuel for the simple reason that the temperature of the unevaporated fuel cannot rise above its boiling point. For the fact that oxidation does not take place in the liquid phase, a number of direct, experimental proofs may be quoted.<sup>2</sup> Tauss and Schulte<sup>3</sup> found that oil vapors showed the same ignition temperature as liquid oil (optimum mixture condition



Kurbelwinkel = crank angle  
 Zündverzögerung = ignition delay  
 Durchbrennen + gesteuerte Verbrennung = complete combustion + directed combustion  
 Nachbrennen = after burning  
 Einspritzbeginn = beginning of injection  
 Zündung = ignition  
 Einspritzende = end of injection  
 eingespritzte Brennstoffmenge = injected fuel  
 unverbrannte Brennstoffmenge im Zylinder = unburned fuel in the cylinder  
 verbrannte Brennstoffmenge = burned fuel

FIG. 268.—Time variation in jet injection and combustion in the Diesel engine: unburned fuel in the cylinder as difference. (From Zinner.<sup>4</sup>)

is presupposed); whereas Schaefer<sup>5</sup> never obtained ignition with Jentsch's ignition-valve tester (which contains three interconnected chambers, into one of which the fuel drips) in the chamber into which the liquid fuel drops, but always in one of the auxiliary chambers. It follows that the evaporation process of the droplets plays a great role. A very fine spray is apparently favorable for a quick evaporation, as are a low boiling point of the fuel and a high air temperature. Influence of air density is qualitatively hard to determine, because great air density

<sup>1</sup> Cf. especially CALLENDAR, *Engineering*, **121** (1926); **123** (1927). KING, R.O., quoted p. 569.

<sup>2</sup> BOERLAGE and BROEZE, "The Science of Petroleum," quoted p. 573.

<sup>3</sup> TAUSS, J., and F. SCHULTE, *Über Zündpunkte und Verbrennungsvorgänge im Dieselmotor*, Wilhelm Knapp, Halle, 1924.

<sup>4</sup> ZINNER, K., *Z. Ver. deut. Ing.*, **82**, 9 (1938).

<sup>5</sup> SCHAEFER, "Werft Reed," *Hafen*, December, 1931.



is, to be sure, favorable because of high heat capacity; but, at the same time, it hinders diffusion of fuel-oil vapor into the gas chamber.

Figure 269 shows schematically, according to Neumann, an analysis of the fuel jet. Dissipation of the fuel jet starts with its exit from the edge of the nozzle and proceeds in the direction of the axis toward the center. Since drop diameter and drop density increase toward the center, the outside portions are preferred for ignition, especially the portions atomized first, which have been in existence for the longest time.

The diameters of the fuel droplets in the jet range themselves around a certain average value, which with good atomization lies in the neighborhood of  $10^{-3}$  cm. In investigation of evaporation of the droplets, direct measurements in multiple-spark photographs, as announced by F.A.F.

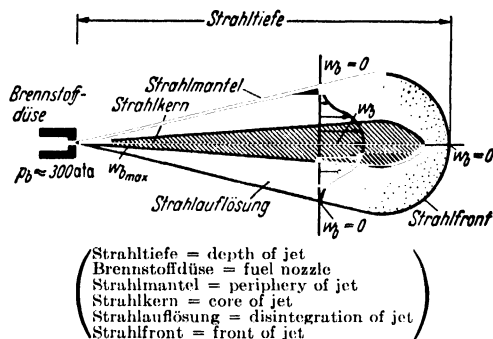


FIG. 269.—Disintegration of the injected fuel jet, schematic.  $w_3$ , velocity of the fuel drops;  $p_0$ , pressure on the liquid fuel during injection. (From K. Neumann.)

Schmidt,<sup>1</sup> would be useful; direct numerical values have not yet been published. Computations have had to serve so far<sup>2</sup> for velocities of droplet evaporation. According to Wentzel, the smaller droplets are said to have largely evaporated in  $\sim 5 \cdot 10^{-4}$  sec, so that, except for very short ignition delays, the evaporation process could play no role at all. Aside from the fact that fundamentally evaporation and oxidation should not be treated separately (cf. also page 585), it must be kept in mind that there are at the basis of these calculations certain assumptions and simplifications through which errors could easily result. An assumption has to be made concerning the movement of drops relative to air (whether this is induced or whether the drops come in contact always with new air), and an average heat conductivity has been used for computation. In a radial-symmetrical problem, however, the average value of heat

<sup>1</sup> SCHMIDT, F.A.F., *Ver. deut. Ing. Forsch.*, 1938, p. 392; cf. also the paper read at the convention of the German Academy of Aeronautical Research, Berlin, 1939.

<sup>2</sup> WENTZEL, W., *Ver. deut. Ing. Forsch.*, 1934, p. 366; *Forsch. Gebiete Ingw.*, **6**, 105 (1935); *Z. Ver. deut. Ing.*, **77**, 908 (1933). Initial work in this direction also by N. Fuchs, *Phys. Z. Sovet.* **6**, 224 (1934).

conductivity over the temperature interval in question cannot simply be taken, but rather an average value commensurate with the problem must be taken, a value most influenced by the colder gas parts in the vicinity of the drops. It is at least imaginable that for this reason the evaporation time calculated by Wentzel might be too short. For a decision, the results of direct observation will have to be awaited.

A description devoid of contradiction of the phenomenon in the engine with consideration of physical and chemical data is easily possible. Ignition takes place, as is apparent, for example, from jet pictures by Nägel (quoted page 575), in general only after the fuel is evaporated. Nevertheless, however, the ignition process will normally not proceed uninfluenced by evaporation, if only for the local cooling effected by evaporation (*cf.* page 584). Even if everything is evaporated, however, the same conditions as in homogeneous gas reaction need not be present (*cf.* page 583); diffusion in particular may enter the picture after evaporation. Assuming (*cf.* a similar estimate, page 49) that one droplet has had a radius of  $10^{-3}$  cm and vapor had to distribute itself by diffusion to a sphere of  $5 \cdot 10^{-3}$  cm radius, the time necessary for this,  $\tau$ , results according to order of magnitude (*cf.* page 286) at  $\sim \frac{(5 \cdot 10^{-3})^2}{2 \cdot 10^{-2}}$ , if we

estimate the diffusion coefficient of the fuel in air under engine conditions at  $\sim 10^{-2}$  cm<sup>2</sup>/sec;  $\tau$  would thus be  $\cong 10^{-3}$  sec and therefore by no means negligible. In agreement with this is the observable fact, to which among others Lindner (quoted page 585) points, that, in general, ignition delays under  $10^{-3}$  sec cannot be measured, according to Schweitzer,<sup>1</sup> even if the fuel is injected into the burning mixture.

The ignition process in the Diesel engine is thus seen to be a complicated interplay of a number of physical and chemical processes that lead to simple relationships only in exceptional borderline cases that are probably never realized in practical operation. In the borderline case of high temperatures,<sup>2</sup> the chemical reaction may be regarded as proceeding with infinite speed, and only the less temperature-dependent physical processes are then responsible for the ignition delay. Connected with this is the small temperature dependence of the ignition delay already remarked upon (*cf.* pages 585ff.) and perhaps the reaching of a limiting value of  $\sim 10^{-3}$  sec (with essential refinement of the spray, it should be possible to go below this limit). Conversely, in the borderline case of low temperatures (which is reached with coal-tar oil under normal conditions, with gas oil and cetene only at very low temperatures),

<sup>1</sup> SCHWEITZER, P.H., *Automotive Ind.*, 1938, p. 848.

<sup>2</sup> Also in the borderline case of easily ignitable Diesel oils under normal operating conditions; for this, it may be said that normally, with cetene numbers above 70, no difference in ignition delays can be found.

chemical reaction will proceed very slowly in comparison with the other processes, and it alone will determine the ignition delay (*cf.* pages 584, 585). Accordingly, under such conditions, pronounced temperature dependence of ignition delay results, corresponding to temperature dependence in homogeneous gas reactions (*cf.* pages 474, 475). In the region of intermediate temperatures that correspond to practical engine operation, the total process should be regarded as a combination of all the different partial processes, and a corresponding intermediate tem-

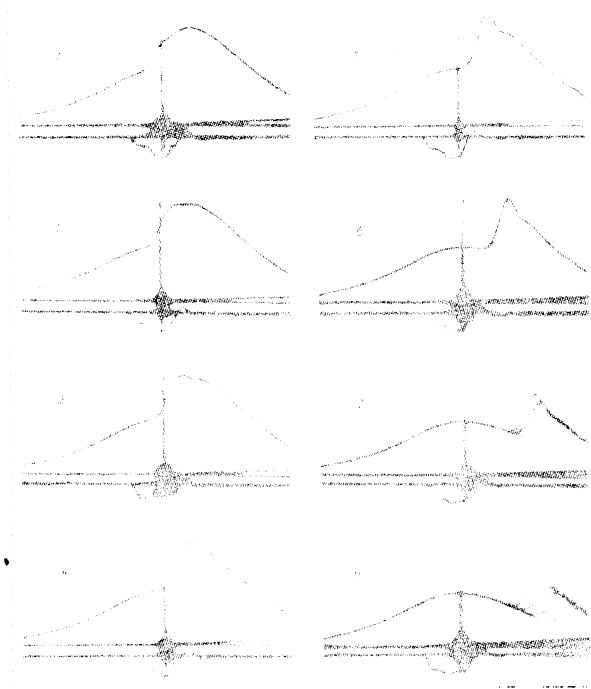


FIG. 270.—Pressure diagrams of the combustion in the Diesel engine with increasing ignition delays (1–8). [From Boerlage and Broeze, *Chem. Rev.*, vol. 22 (1938).]

perature coefficient is observed, which, however, is essentially smaller than in homogeneous gas reaction. For these reasons, we shall hardly succeed in maintaining the great temperature dependence of the ignition delay in the ignition of liquid injected fuels (even gasolines; Lindner, quoted page 585), as is obtained in ignition in homogeneous gas phase (Tizard and Pye, quoted page 472; Jost and Teichmann, quoted page 475).

In considering the interplay of physical and chemical processes in ignition in the Diesel engine in the manner indicated, we naturally arrive at an understanding of the observed phenomena. Of course, this context excludes the comprehension of the entire field of phenomena by means of a simple formula.

The longer the ignition delay, the less favorable is the efficiency. Figure 270 shows (according to Boerlage and Broeze) a number of indicator diagrams with increasing ignition delays. With increasing ignition delay and ignition only after upper dead center, pressure decrease occurs progressively (in consequence of expansion) before ignition. This special diagram shows that, with very long ignition delays, the remaining mixture does not have to react instantaneously with knocking. In spite of the long delays, pressure rises here are normal; the speed of the pressure

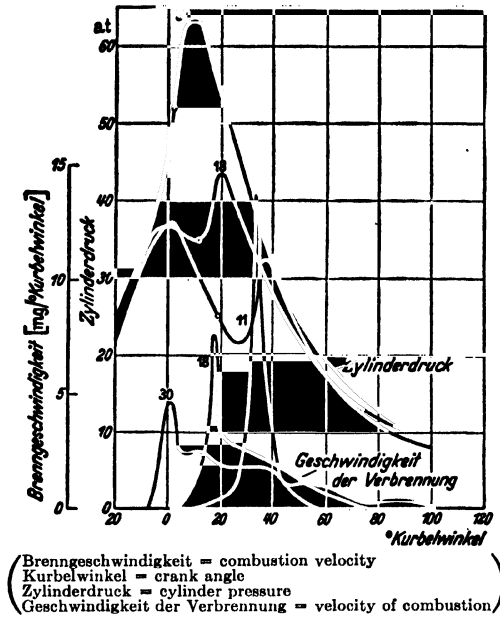


FIG. 271.—Influence of the beginning of injection (in ° of crank angle before upper dead center; given at the various curves) on pressure development and combustion velocity; 0, moment of the end of jet injection. (From Rothrock and Selden, p. 580.)

rise first increases with increasing delay and drops again. The smaller pressure rise under protracted delays (piston already at a greater distance from upper dead center) is partly conditioned by the quick volume extension in this phase. Figure 271 shows cylinder pressure and the speed of combustion for different periods of initial injection as a function of the crank angle. We can see that an after-burning still takes place a considerable time after the end of the injection. Rothrock and Selden point out that a considerable loss of output is connected with this. K. Neumann had previously pointed this out and attempted a reaction-kinetic treatment<sup>1</sup> (cf. page 588).

<sup>1</sup> NEUMANN, K., *Forsch. Gebiete Ingw.* 5, 173 (1934); 7, 57 (1936). Paper read at the Convention of the German Academy of Aeronautical Research, Berlin, 1939.

**3. Practical Determination of Ignitibility of Diesel Fuels.**—The details in the methods of determination of ignitibility of Diesel fuels lie again outside the scope of this book.<sup>1</sup> The best method in this case is a test engine. In order to be independent of special engine conditions, a mixture of cetene ( $C_{16}H_{32}$ , a very ignitable normal olefin) and  $\alpha$ -methyl naphthalene (a very inert aromatic) has been chosen for a scale of comparison. Fundamentally, the same misgivings exist for the cetene scale as for the octane scale, with the additional fact here that ignition delay also depends on the evaporation process (page 580). Besides experiments in an actual engine, numerous measurements of ignition delays in bombs have been made. Even if the engine conditions cannot be completely duplicated here, still it is much easier than in the Otto

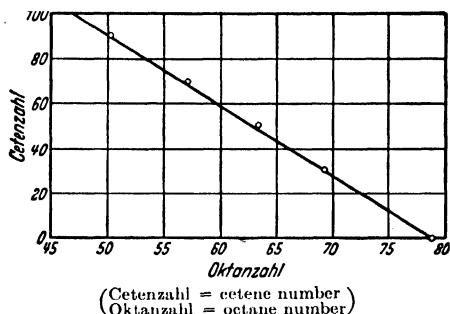


FIG. 272.—Cetene numbers and octane numbers of various fuels. (From *Dumanois*, p. 560.)

engine to obtain significant experimental results of which we shall make extensive use in our discussion. In any case, it is easier to work with a test bomb with well-defined *temperatures and pressures* than with an engine. Measurements with ignition testers<sup>2</sup> are much more dubious, since, in these, conditions deviating fundamentally from engine conditions are realized, *i.e.*, low pressure, influences of the walls, very long induction time, etc., as far as they are said to be at all measurable. Results thus gained are not usable for quantitative relations, even if the results can be of practical use under careful evaluation. It should probably be stressed that it is fundamentally impossible to compensate for the low pressure in the ignition tester (compared with the engine) by means of a higher relative oxygen concentration.

If the assumption is true that, in case of ignition in the Diesel engine, the same chemical reactions occur as in knocking in the Otto engine,

<sup>1</sup> Cf. the report by P.H. Schweitzer [*Chem. Rev.*, **22**, 107 (1938)], which summarizes all findings; also the papers of the VDI meeting "Motor- und Kraftstoff," 1938.

<sup>2</sup> Cf. in this connection HELMORE, W., "The Science of Petroleum," Vol. IV, p 2970, 1938. JENTSCH, H., *Z. Ver. deut. Ing.*, **68**, 1150 (1924). SCHAEFER, D., *Proc. World Petroleum Congress*, Vol. II, p. 218, London, 1938.

a relationship should exist between octane and cetene numbers of fuels. This, to be sure, was found by Boerlage and Broeze. Since, in general, a fuel is suitable for Diesel operation in proportion to the ease with which it ignites (a property that is unsuitable for the Otto engine) an inverse course of octane and cetene numbers results.<sup>1</sup> In Fig. 272, a presentation according to Dumanois<sup>2</sup> is given. That the relation between cetene numbers and octane numbers is linear may be more accidental, if for no other reason than that for Diesel combustion different boiling behavior may be of considerable influence. The clearly diametrically opposed behavior of the two quantities is definite and very characteristic.

TABLE 121.—IGNITION BEHAVIOR OF PURE SUBSTANCE

| Substance              | Formula                         | Ignition delay in degrees of crank angle at pressures of |        |                       |
|------------------------|---------------------------------|--|--------|-----------------------|
|                        |                                 | 30 atm   | 15 atm | 10 atm                |
| <i>n</i> -Heptane..... | C <sub>7</sub> H <sub>16</sub>  | 7.1  | 12.8   | 21.2·10 <sup>-3</sup> |
| Cetene.....            | C <sub>16</sub> H <sub>32</sub> | 6.3  | 10.5   | 18.7                  |
| Cetane.....            | C <sub>16</sub> H <sub>34</sub> | 6.0  | 10.2   | 18.3                  |
| Tetatriacontadien..... | C <sub>14</sub> H <sub>66</sub> | 8.4  | 13.6   | 20.3                  |

Since, within homologous series (*e.g.*, that of the *n*-paraffins), boiling point, speed of thermal decomposition (cracking), oxidation tendency, knocking tendency, and ignitibility in the Diesel engine all change in the same direction, it is possible to find parallels between each pair of these magnitudes.<sup>3</sup> In comparison of substances not from homologous series, of course, there will not longer be a perfectly parallel change between boiling point and ignitibility; but more or less valid approximate relations can be obtained when the different composition (at identical boiling behavior) is comprehended by any other physical magnitude that is especially sensitive to a change in the action of (hard to ignite) aromatics. As such further determining magnitudes, densities, fraction indices, aniline points, and parachor (a combination of surface tension and density) have been adduced<sup>4</sup> and with them Diesel indices (or similarly named measurements) have been formulated that are quite well suited for orientation of fuels of normal composition. Since magnitudes that

<sup>1</sup> BOERLAGE, G.D., and J.J. BROEZE, *Ver. deut. Ing. Forsch.*, 1934, p. 366.

<sup>2</sup> DUMANOIS, P., "The Science of Petroleum," Vol. IV, p. 3054.

<sup>3</sup> Concerning decomposition tendency, cf. Boerlage and Broeze, quoted p. 497; also *J. Inst. Petroleum Tech.*, **21**, 40 (1935); and JOST, W., L. v. MÜFFLING, and ROHRMANN, *Z. Elektrochem.*, **42**, 488 (1936).

<sup>4</sup> Cf. SCHWEITZER, P.H., quoted p. 580. HEINZE, R., *Braunkohle*, **34**, 639 (1935). MARDER, M., and P. SCHNEIDER, *Automobillech. Z.*, **40** (1937), etc.

have no direct causal connection have sometimes been combined, however, occasionally considerable deviations have resulted.

It becomes clear, for example, from a series of measurements by Boerlage and Broeze (quoted page 571) that, as has often been observed, besides chemical reactivity, ease of evaporation plays a role in the ignitibility of Diesel oils (Table 121).

The fact that heptane is harder to ignite than cetene and cetane is probably a result of the smaller reactivity of the shorter chains; but the fact that tetratriacontadien, in turn, is even harder to ignite than cetene seems to point to an inhibition of the reaction by too slow an evaporation. This behavior is marked in the relations between boiling point and cetene number which Pier<sup>1</sup> reports for paraffin base, mixed-base, and asphalt-base gas oils. Up to an average boiling point of about 300°C, the cetene number rises with the boiling point. With further rise, it drops again. With the lower temperature, the influence of reactivity of hydrocarbons, which increases with increasing molecule size, predominates. With higher temperatures, the increasingly more difficult evaporability opposes this influence.

TABLE 122.—CETENE NUMBERS OF GAS OILS AND RESIDUES OF VARIOUS CRUDE OILS  
(FROM BOERLAGE AND BROEZE)

| Crude oil | Cetene number    |                         |
|-----------|------------------|-------------------------|
|           | Gas-oil fraction | Residue                 |
| A         | 60               | 44                      |
| B         | 58-60            | 44                      |
| C         | 58-60            | 32                      |
| D         | 47-49            | 26                      |
| E         | 24               | 39                      |
| F         | 30-33            | 24                      |
| G         | 27               | (total crude oil)<br>15 |

That evaporation can be of essential influence is suggested by the table given (Boerlage and Broeze<sup>2</sup>). The cetene numbers of the gas-oil fractions obtained from different crude oils as well as the cetene numbers of the residue with its higher boiling point have been given. In many cases, the cetene numbers of these substances are essentially lower than those of gas oil (Table 122).

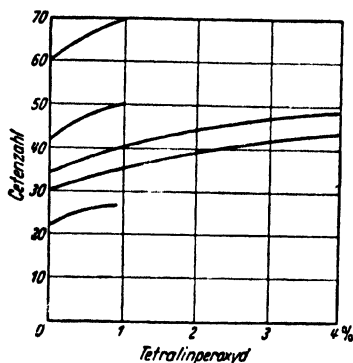
Many substances that induce knocking in the Otto engine promote ignition in the Diesel engine. References to this are numerous in the

<sup>1</sup> PIER, M., Paper read at the Convention of the German Academy of Aeronautical Research, Berlin, May, 1939.

<sup>2</sup> BOERLAGE and BROEZE, "The Science of Petroleum," quoted p. 573.

literature; usually the same substances are mentioned that induce knocking—organic nitrites, peroxides, etc.; but there is no mention of whether such additions have proved effective in practical operation. Since the influence of additions on knocking can vary according to the constitution of the fuel, the same may be expected of Diesel oils. It stands to reason that the susceptibility of hard to ignite coal-tar oils is not very great (cf. the discussion of different lead sensitivity of gasolines, Chap. XII, pages 540ff.). Furthermore it should be considered that additions of small quantities could, of course, influence only the chemical reaction; but if the evaporation process should be of importance in Diesel ignition, nothing can be changed by additions of small quantities.

Boerlage and Broeze<sup>1</sup> give some numerical evidence of the effectiveness of additions. Figure 273 shows the influence of tetraline peroxide on the cetene number of different Diesel oils. To a certain extent, Fig. 273 shows an analogy to the effect of lead on paraffins (Chap. XII, pages 562ff.). The increase of the cetene number by the same addition is higher the higher the cetene number of the oil was. Table 123 shows a similar effect, namely, that of previous treatment with ozone; in this, formation of peroxide-like substances is probable.



(Cetenzahl = cetene number  
Tetralinperoxyd = tetralineperoxide.)

FIG. 273.—Effect of variously high additions of tetralineperoxide on the cetene numbers of various Diesel fuels. (From Boerlage and Broeze.)

TABLE 123.—CETENE NUMBERS OF VARIOUS DIESEL OILS (FROM BOERLAGE AND BROEZE)

|                             |    |    |    |    |    |    |
|-----------------------------|----|----|----|----|----|----|
| Before ozone treatment..... | 51 | 49 | 44 | 44 | 40 | 40 |
| After ozone treatment.....  | 70 | 52 | 70 | 44 | 46 | 40 |

**4. Reaction-kinetic Treatment of the Ignition Process in the Diesel Engine.**—For various reasons, a reaction-kinetic treatment of the ignition process in the Diesel engine offers difficulties. Very confusing conditions are created by the fact that a heterogeneous system has to be dealt with and that there are inside the jet core unevaporated cold fuel and no air; whereas toward the outside the relative influence of the air and temperature becomes increasingly greater, and in the beginning fuel is still

<sup>1</sup> BOERLAGE and BROEZE, "The Science of Petroleum," quoted p. 573.



present in liquid form. Qualitatively this much is clear—and experience bears it out—that ignition will begin in a certain area of the jet (namely, in the vicinity of the edge) where fuel concentration is still high enough, simultaneously enough air is present, and conditions of temperature and drop evaporation are not too unfavorable. At all events, however, ignition takes place in a range where neither temperature nor fuel concentration is exactly known. Furthermore, at least in principle, a heterogeneous reaction cannot be completely ruled out; *cf.* the previously mentioned experiments (page 569), especially those by Callendar and R.O. King. It is of importance that during evaporation the remaining droplets may be enriched by more easily ignited, higher boiling component parts. To be sure, we should like to assume that, under conditions of normal Diesel operation, conditions for heterogeneous reaction are not very favorable; for, with temperatures of perhaps 500°C and above in the gas, a steady, very active evaporation from the drop surface will take place. Thus exactly those molecules which could react at the border area are constantly removed from it. Moreover, because of this evaporation, the oxygen concentration in this border area must be relatively low or may even be practically zero (pages 574,ff.). A mathematical treatment of droplet evaporation, as has been repeatedly tried, for instance, by Wentzel, (page 576), offers fundamental difficulties.

Connected with the same problems is another basic difficulty. If a droplet moves relative to the surrounding air until it is completely evaporated, there will not be anywhere a considerable volume with comparatively high fuel concentration. There will then be no opportunity at all for real ignition; although, in the high pressures and temperatures of the Diesel engine, fuel will react under unfavorable conditions and even cause the frequently observed (reported among others by Boerlage and Broeze) pressure rise just before the real ignition. To a certain extent, however, the same difficulty remains even if the drops evaporate in quiet air. If a drop of  $10^{-4}$  cm radius evaporates in air which under normal conditions has been tenfold compressed, the fuel quantity is sufficient for a stoichiometric mixture in a sphere of  $3.5 \cdot 10^{-3}$  cm radius, *i.e.*, a very small sphere. For the auto-ignition of this very small sphere, considerations hold true analogous to those made with regard to heat explosion and spark ignition (page 47). Since heat is conducted by the imagined limits of this sphere to the surrounding air and since active particles present diffuse away from it to the air, there results for such a small volume, exactly as in the earlier examples, a very unfavorable, high "ignition temperature," which may be several hundred degrees higher than that calculated for larger volumes. Therefore an area in which an isolated little drop has evaporated is not suitable for ignition, but only those areas are suitable in which either larger drops or a number

of smaller drops have evaporated.<sup>1</sup> Practically this is probably only in an area in which in close proximity a large number of small drops have evaporated, because their evaporation takes place more quickly than that of large drops. For a mathematical treatment of evaporation, that is likewise of importance; for, in areas where many drops evaporate simultaneously, it cannot be assumed that there is an infinite surplus of air for every drop. The cooling of the air because of evaporation in this area should by no means be neglected. Since, as we have seen earlier (page 526), in a closed chamber any local cooling makes itself felt in the entire space, for practical operation this cooling (from the walls as well as from the jet) might well make a difference. Rothrock and Selden (cited page 589) proved (by the pressure decrease of  $\sim 5$  per cent) cooling in consequence of fuel injection in nitrogen (*i.e.*, without oxidation reaction). Cooling through the incoming and evaporating fuel jet at the edges of the jet in which ignition starts has been measured directly by Lindner; it can assume considerable values  $\sim 100^\circ\text{C}$ . From this, it is directly clear that a transfer of reaction-kinetic relations from homogeneous gas reactions to the ignition process in the Diesel engine is by no means permissible.<sup>2</sup>

Evaporation and oxidation of the fuel probably take place simultaneously. Definite reaction-kinetic statements can be made at the outset only for borderline cases. Of all the factors cooperating in ignition in the Diesel engine—jet atomization, heating up of the drops, evaporation of the drops, and oxidation of the evaporated fuel—oxidation certainly shows the greatest temperature dependence (apparent activation energy about 30 to 40 kcal; *cf.* pages 474, 475, and 448*ff.*). If vapor pressure is the decisive value for droplet evaporation, a much smaller temperature dependence results (apparent activation energy  $\sim 10$  kcal), and the other influences show an even smaller dependence on temperature (at the most, corresponding to a low power of absolute temperature). In consequence, the following can be predicted with certainty: The chemical reaction characterized by the highest temperature coefficient must proceed so quickly at high temperature that the observed ignition delay becomes practically independent of it; whereas, conversely, at low temperatures its speed is so slow that it alone determines the time.<sup>3</sup> The range in which chemical reaction alone determines the time is practically reached probably only in the case of hard to ignite coal-tar

<sup>1</sup> One reason for this is that the combustion could not spread from there to the surroundings even if it had started.

<sup>2</sup> LINDNER, W., Paper read at the Convention of the German Academy of Aeronautical Research, Berlin, May, 1939.

<sup>3</sup> W. Jost, paper read at the VDI Convention Motor und Kraftstoff, Augsburg, September, 1938; published in *Proc. Ver. deut. Ing.*

oils; whereas it seems that, with easily igniting gas oils, the range is easily reached in which ignition delay becomes practically independent of reaction velocity. This follows from the frequent findings that, above a certain cetene number (*e.g.*, 55 to 70), the observed ignition delay becomes independent of the cetene number.

Experiences in the engine and in research bombs agree well with these statements. In Fig. 274, we give Müller's<sup>1</sup> experimental results of gas oil, soft-coal tar oil, hard-coal tar oil as well as of pure cetene and  $\alpha$ -methyl naphthalene. For the given ignition delay, the values obtained for lower temperatures are smaller than those of other authors, which

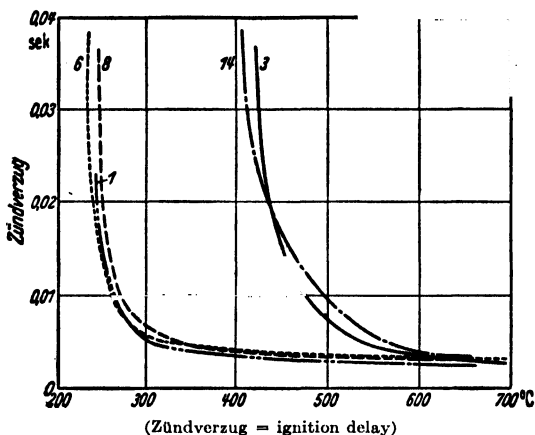
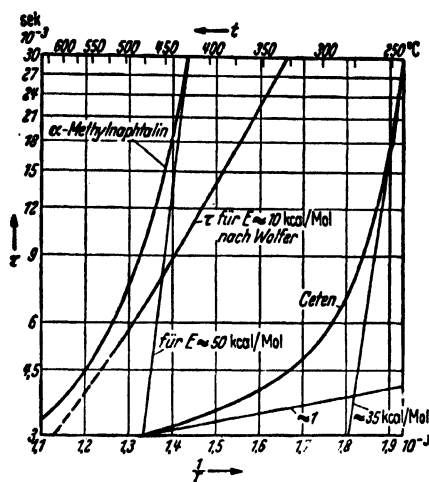


FIG. 274.—Ignition delays in the ignition of various oils in an experimental bomb with an air density of  $10 \text{ kg m}^3$ . 1, cetene. 3,  $\alpha$ -methyl naphthalene. 6, gas oil. 8, soft-coal tar oil. 14, hard-coal tar oil. (From R. Müller.)

must be due to the method employed. Independent of a correction that may be necessary for the temperatures, however, the following statements are true: Gas oils and soft-coal oils fall into one group, with only slightly deviating ignition delays, together with the standard fuel, cetene; whereas hard-coal tar oils (essentially of aromatic character) behave like  $\alpha$ -methyl naphthalene. Since temperature dependence is different for the individual substances, partial overlapping, as observed elsewhere, may occur. Figure 274 shows that, with higher temperatures—in gas oils and soft-coal tar oils from  $\sim 400^\circ\text{C}$  on—temperature dependence of the ignition delays is only extraordinarily small, smaller by far than it should be if it were conditioned by a chemical reaction. This observation, which is generally made—even though sometimes only with higher temperatures—may be explained by the fact that, with sufficiently high temperatures, the chemical reaction occurs so quickly

<sup>1</sup> MÜLLER, R., *Kraftfahrtechnische Forschungsarbeiten*, **3**, 1 (1936).

that it practically no longer plays a role in the velocity. This becomes even clearer from the graphs in Fig. 275, where (again according to



( $\tau$  für  $E$  . . . nach Wolfer =  $\tau$  für  $E$  . . . according to Wolfer)

FIG. 275.—Logarithmic presentation of the experimental results of Müller (log of ignition delay,  $\tau$ , against reciprocal absolute temperature); also, experimental results of Wolfer (p. 578). Given in the figure are the apparent activation energies  $E$ , which result from the various curve slopes.

Müller's experiments) the logarithms of the ignition delays of cetene and  $\alpha$ -methyl naphthalene are plotted against the reciprocal absolute temperature. With low temperatures, temperature dependence prevails, as corresponds to chemical reaction. From the slopes of the curves, values of apparent activation heats of  $\sim 35$  kcal for cetene and  $\sim 50$  kcal for  $\alpha$ -methyl naphthalene result, which correspond approximately to the activation energies found otherwise for aliphates and aromatics (page 475). As the limiting value of activation energy for higher temperatures, values of only  $\sim 1$  kcal are found; that is so little that a chemical reaction cannot possibly be responsible for it.

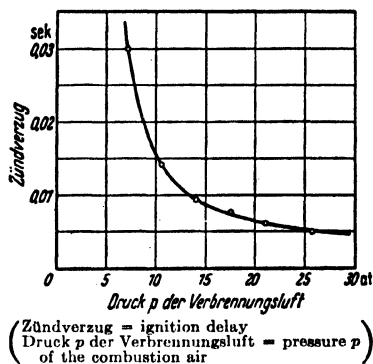


FIG. 276.—Dependence of the ignition delays of a Diesel oil on pressure. (From Wolfer, p. 578.)

The ignition delay decreases with increasing pressure, and it decreases a little more than with the inverse first power of compression.<sup>1</sup> Figure

<sup>1</sup> SCHMIDT, F.A.F., and H.H. WOLFER, *Ver. deut. Ing. Forsch.* 392, 1938.

276 shows experimental values by Wolfer. The pressure dependence of the ignition delay corresponds to about  $1/p^{1.19}$ .

**5. Further Reaction-kinetic Observations on Combustion in Diesel Engines.**—The ideal combustion process in the Diesel engine would presuppose that the ignition delay could be neglected and that the further combustion takes place exactly to the degree that the fuel is injected. Any delay of reaction upon injection means a loss of useful pressure and thus of efficiency. These questions have been theoretically as well as practically treated, especially by K. Neumann.<sup>1</sup> Conversely, Neumann also deduced the chronological course of the reaction velocity from the

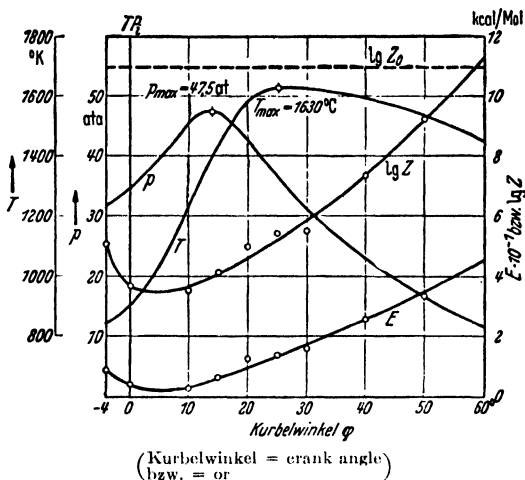


FIG. 277.—Kinetic analysis of the course of combustion in the Diesel engine.  $p$  and  $T$  measured pressure and average temperature as a function of the crank angle;  $E$  and  $Z$  apparent activation energies and shock numbers of the chemical reaction derived from them.  $Z_0$  would be the determining shock number with completely evaporated and thoroughly mixed fuel. (From K. Neumann.)

indicated pressure course in a Diesel engine when the injection law is known. The course of the reaction may be analyzed only if a simplified kinetic law is assumed; bimolecular reaction between (homogeneously distributed, gaseous) fuel and air-oxygen is indicated by Neumann. This assumption is, of course, not fulfilled in reality, but the comparison of the velocity constants computed for it with those to be expected for a gas reaction of the second order allows conclusions as to the conditions in the engine. Figure 277 shows the measurements derived by Neumann from an actual engine. From the empirical reaction velocities, "constants" for reaction of the second order have been computed; these,

<sup>1</sup> NEUMANN, K., *Forsch. Gebiete Ingw.* **5**, 171 (1934); **7**, 57 (1936); also the paper read at the convention of the German Academy of Aeronautical Research, Berlin, 1939; published in *Schriften deut. Akad. Luftfahrtforsch.*

written down in the form of shock number times Boltzmann factor (with use of empirical temperature dependence) and the value of the apparent shock numbers  $Z$  and of the apparent activation energies  $E$ , are represented in Fig. 277. Corresponding to the small temperature dependence of the reaction velocity found (1 to 7 per cent velocity increase for 10 per cent temperature rise), the apparent activation energies in a wide range are very low and are—like the “shock number”—by no means constant. All this can be correctly understood only if a homogeneous gas reaction is not present. Here again the same situation that played a role in the ignition process becomes apparent, namely, droplet evaporation and mixture formation cannot be neglected in the total process.<sup>1</sup> The fact that the “shock number” calculated from the kinetic equation remains lower by  $10^6$  below the gas-kinetic value is the same as is apparent in Wolfer's and F.A.F. Schmidt's equations for the ignition delay. It must apparently come from the fact that drop evaporation and mixture process determine the velocity to a great extent.<sup>2</sup> If we therefore intend to increase reaction velocity (and thus efficiency), we should work mainly for better mixtures. That, essentially, is also Neumann's reasoning.

Spectroscopic investigations show also that combustion in the Diesel engine largely takes place with inadequate mixture. In combustion of well-mixed fuels with air, with not too much fuel excess, the usual band spectra are obtained (Chap. VII). In not thoroughly mixed gases, we obtain, just as in the Diesel engine in consequence of carbon deposit, a continuous temperature brightness.<sup>3</sup>

In this connection, we refer to Rothrock and Selden,<sup>4</sup> especially also Fig. 271, page 579, which shows the long post-combustion periods observed in fast-running Diesel engines; the authors regard the avoidance of this long post-combustion as the most important single factor in the development of the Diesel engine. In this, the time-deciding factor is probably the mixture (not the evaporation, according to Rothrock and Selden). Thus it is chiefly constructional features that can lead to

<sup>1</sup> In evaluating the results in Fig. 277, it must, of course, be kept in mind that in computation only average temperatures can be used and these may vary widely locally; that fuel and oxygen concentration are subject to wide local variations need not be especially stressed. Local combustion temperatures in Diesel engines have meanwhile been optically measured by K. Neumann, in a paper read in German Academy of Aeronautical Research.

<sup>2</sup> Since the combustion process is certainly not a simple bimolecular reaction, agreement with the theoretical equation need not prevail from the start; but, in the cases of a gas reaction with chain-branching, deviations would be expected exactly in the opposite direction—shock numbers apparently too high.

<sup>3</sup> Cf. in this connection NEUMANN, quoted p. 587; also BECK, G., and C. EIRCHSEN, *Ver. deut. Ing. Forsch.*, 1936, p. 377. KARDE, K., Dissertation at Hanover, 1936.

<sup>4</sup> ROTHROCK, A.M., and R.F. SELDEN, *Chem. Rev.*, **22** (1938).

improvement, not those concerned with the combustion process or the fuel.

We should like to assume, anyway, that progress of the Diesel engine will not depend to the same extent as in the Otto engine on the achievements of the fuel chemist. That has its deeper reason in the fact that the same factors that increase performance, especially the increase of the compression ratio, influence combustion behavior in the Diesel engine favorably; whereas in the Otto engine they have an unfavorable effect on knocking. If, therefore, the creation of high-grade fuels is decisive, it seems to be fundamentally possible that in the Diesel engine all problems will be solved from the purely constructional approach.<sup>1</sup>

<sup>1</sup> For example, the combustion of hard-coal tar oil in Diesel engines is possible by means of purely constructional measures which, in the last analysis, bring about an increase in temperature (*cf.* Zinner, quoted p. 571).

## COMPREHENSIVE WORKS IN THE FIELD

Since a complete bibliography was not aimed at in the present volume, comprehensive works are here given from which the reader can obtain further information in the field.

### A. MONOGRAPHS AND HANDBOOKS, CONVENTION REPORTS

- BAILEY, K.C.: "The Retardation of Chemical Reactions," London, 1937. Contains an extensive, though not critical, compilation of works on the inhibition of chemical reactions, on oxidation processes in the gas and liquid phase, as well as on the knocking process; with a large bibliography.
- BONE, W.A., and D.T.A. TOWNEND: "Flame and Combustion in Gases," London, 1927.
- BONE, W.A., D.M. NEWITT, and D.T.A. TOWNEND: "Gaseous Combustion at High Pressures," London, 1929.
- ELLIS, C.: "The Chemistry of Petroleum Derivatives," Vol. II, New York, 1937, with a good survey on oxidation processes and a large bibliography.
- ELLIS, O.C. DE C.: "A History of Fire and Flame," 1932.
- ELLIS, O.C. DE C., and W.A. KIRKBY: "Flame," Methuen, London, 1936.
- ENDRES, W.: "Der Verbrennungsvorgang im Gas- und Vergasermotor," Berlin, 1928.
- "Handbuch der Feuer- und Explosionsgefahr," Feuerschutzverlag Ph. L. Jung, Munich, 1936.
- LEWIS, B., and G.V. ELBE: "Combustion, Flames and Explosions of Gases," Cambridge, 1938.
- LINDNER, W.: "Entzündung und Verbrennung von Gas- und Brennstoffdampf-gemischen," Berlin, 1931.
- MACHE, H.: "Die Physik der Verbrennungserscheinungen," Leipzig, 1918.
- NASH, A.W., and D.A. HOWES: "The Principles of Motor Fuel Preparation and Application," 2 vols., London, 1934-1938.
- PRETTRE, M.: L'Inflammation et la combustion explosive en milieu gazeux, 2 parts, Paris, 1933 and 1934.
- PRETTRE, M.: Réactions en chaînes, 2 vols, Paris, 1936.
- PYE, D.R.: "Brennkraftmaschinen," Berlin, 1931.
- RIBAUD, G.: Températures des flammes: rayonnement des gaz incandescents et des flammes, Paris, 1930.
- RICARDO, H.R.: "Schnellaufende Verbrennungsmotoren," Berlin, 1932.
- SCHUMACHER, H.J.: "Chemische Gasreaktionen," Dresden, 1938.
- SEMENTOFF, N.: "Chemical Kinetics and Chain Reactions," Oxford, 1935.
- SERRUYS, M.: La Combustion détonante dans les moteurs à explosion, *Pub. sci. tech. ministère air*, 103, 1937.
- SERRUYS, M.: Etude expérimentale de l'allumage par point chaud dans les moteurs à explosion, *Pub. sci. tech. ministère air*, 115, 1937.
- "The Science of Petroleum," Vol. IV, Oxford, 1938, with the following contributions:
- BEALE, C.O.B.: The Engineering Aspects of Detonation.
- BEATTY, H.A., and G. EDGAR: Theory of Knock in Internal-combustion Engines.
- BOERLAGE, G.D., and J.J. BROEZE: Combustion Research in Compression-ignition Engines.



CALINGAERT, G.: Anti-knock Compounds.

CAMPBELL, J.M. and T.A. BOYD: Measurement of the Knocking Characteristics of Automotive Fuels.

DUMANOIS, P.: Recherches Detonation in France.

EGERTON, A.C.: General Statement as to Existing Knowledge on Knocking and Its Prevention.

FRASER, R.P.: Flame Propagation, Particularly with Reference to Vibratory and True Detonation Flames.

GARNER, F.H.: Lead Susceptibility of Gasoline.

HELMORE, W.: Spontaneous Ignition Temperatures: Determination and Significance.

LAFFITTE, P.F.: Flames of High-speed Detonation.

LOVELL, W.G., and J.M. CAMPBELL: Knocking Characteristics and Molecular Structure of Hydrocarbons.

MARDLES, E.W.J.: Oxidants and Anti-oxidants in the Petroleum Industry.

MAXWELL, G.B., and R.V. WHEELER: Ignition and Flame Movement.

NEWITT, D.M., and D.T.A. TOWNEND: Combustion Phenomena of Hydrocarbons.

NEWITT, D.M., and D.T.A. TOWNEND: Combustion Phenomena at High Pressures.

NEWITT, D.M., and D.T.A. TOWNEND: Ignition in Gases with Special Reference to Knock Problems.

PRETTRE, M.: The Susceptibility to Oxidation of Internal-combustion Engine Fuels and Their Tendency to Produce Knocking in Engines.

STANSFIELD, R.: The Correlation of Road and Laboratory Knock Ratings of Motor Fuels.

UBBELOHDE, A.R.: Processes of Slow Oxidation Leading to Ignition.

Numerous references on the behavior of fuels, oxidation, and knocking can be found in the *Annual Reviews of Petroleum Technology* published by the Institute of Petroleum, Vols. 1-3, 1936-1938.

On engine combustion in general, see a number of the monographs that have appeared in the series of *VDI-Forschungshefte*, Berlin VDI-Verlag. See also the addresses of the fall convention of the VDI in Augsburg, 1938.

For combustion in the Diesel engine, see especially the series "Dieselmaschinen" of the VDI, Nos. 1-7, Berlin, 1924-1938.

For the most recent developments, see especially the papers at the convention of the Deutsche Akademie der Luftfahrtforschung, Berlin, May, 1939, to appear in the publications of the Deutsche Akademie der Luftfahrtforschung.

For the entire field of combustion in the gas phase, see further the papers of the American Symposium on Gaseous Combustion, *Chem. Ind. Rev.*, Vols. 21 and 22 (1937/38), as well as the corresponding papers at the Bunsen convention, 1936, *Z. Elektrochem.*, Vol. 42 (1936).

For the reactions of ions in gases not treated here, see G. Glockler and S.C. Lind, "The Electrochemistry of Gases and Other Dielectrics," Chapman and Hall, London.

BRÜCKNER, H.: "Gastafeln, physikalische, thermodynamische und brenntechnische Eigenschaften der Gase und sonstigen Brennstoffe," R. Oldenbourg, Munich and Berlin, 1937.

## B. INDIVIDUAL WORKS

FUHRMANN, E.A., and H. KÖTTGEN: Darstellung und Temperatur stehender Kohlenstaub- und Kohlenstaub-Gasexplosionen, *Z. physik., Chem.*, Sec. A, **169**, 388 (1934).

- KONEN, H., and E. MATHES: Bibliographie der wissenschaftlichen Literatur über Schlagwetter und Kohlenstaubexplosionen, sowie verwandter, die Gefahren des Bergbaus betreffenden Fragen, 1933.
- LEWIS, B., and G. v. ELBE: Zur Knallgasverbrennung, *J. Am. Chem. Soc.*, **61**, 1350 (1939).
- MÜLLER-HILLEBRAND, D.: Explosionsprüfungen schlagwettergeschützter elektrischer Geräte, *Elektrizität im Bergbau*, **13**, 69 (1938).
- SEEBER, F.: Dissertation at Breslau, 1932, *Luft.-Forsch.*, **12**, 161 (1936); **16**, 18 (1939).
- WEINHART, H.: *Luft-Forsch.*, **16**, 74 (1939).
- WITHROW, L., G.M. RASSWEILER: Studying Engine Combustion by Physical Means, *J. Applied Phys.*, **9**, 362 (1938).

The comprehensive reviews on combustion by B. Lewis, *Chem. Ind. Rev.*, **10**, 49 (1932), as well as W. Jost, *Z. Elektrochem*, **41**, 183, 242 (1935).

Detailed bibliographies of the older literature, especially on hydrocarbon combustion, can be found in

- PRETTRE, M.: *Ann. Office nat. des combust. liquides*, **6**, 269, 533 (1932); **7**, 699 (1932); *Bull. soc. chim. France*, (4), **51**, 1932 (1932).
- BURKE, S.P., C.F. FRYLING, T.E.W. SCHUMANN: *Ind. Eng. Chem.*, **24**, 804 (1932).
- WILKEN-JORDEN, T.J.: *J. Chem. Soc. S. Af.*, **32**, 248, 283, 322 (1932).
- CLARK, A.L., and W.C. THEE: *Ind. Eng. Chem.*, **17**, 1219 (1928).

For engine combustion, especially knocking, cf. also the *Proceedings of the World Petroleum Conference*, as well as the series, *Kraftfahrttechnische Forschungsarbeiten*, VDI-Verlag, Berlin.

For combustion power engines, cf. also the abstract by W. Meissner and T. Schinnerer in *Die Physik in regelmässigen Berichten*, **7**, 93 (1939) (No. 3, p. 5). VDI-Verlag, Berlin.



## NAME INDEX

- Aivazov, B. V., 388, 444, 454  
 Allen, A. O., 10  
 Allum, 410  
 Alyea, H., 291, 295, 301, 380  
 Amdur, 316  
 Amiel, J., 468  
 Andreew, E. A. (Andreev), 416, 444, 451  
 Andrew, J., 401  
 Anwandter, R., 72  
 Appin, A., 20  
 Arsdell, P. M. van, 442  
 Askenasay, 46  
 Askey, J., 378  
 Aubert, M., 443  
 Autridge, L. E., 371  
 Avramenko, L., 229, 322  
 Awbery, J. H., 220, 223, 240  
  
 Bach, 437  
 Backström, 380  
 Bailey, K. C., 567  
 Banks, F. R., 559  
 Barak, M., 317, 463  
 Baret, 290  
 Baron, M., 388  
 Bates, J. R., 317, 489  
 Bawn, E. D. H., 342, 374  
 Bay, Z., 316  
 Beale, C. O. B., 591  
 Beatty, H. A., 380, 454, 498  
 Beck, G., 233, 589  
 Beck, van der, 382  
 Becker, A., 366  
 Becker, R., 142, 237  
 Becker, R., 163, 199, 206  
 Belchetz, 418  
 Belinfante, A. H., 135  
 Bell, J., 233  
 Benedikt, W. S., 372  
 Bennet, 462  
 Bergmann, L., 9  
 Berl, E., 130, 462, 466, 499, 548  
 Berlin, 554  
  
 Berthelot, M., 161, 284  
 Best, H. W., 570  
 Beutler, H., 236  
 Biron, A., 297  
 Bisand, L., 240  
 Blair, 405  
 Bloch, 35  
 Bloch, A. M., 422  
 Bodenstein, M., 258, 292, 316, 317, 334,  
 380, 391  
 Boerlage, G. D., 394, 497, 514, 573,  
 583  
 Böeseken, 409  
 Bogdandy, St. von, 236  
 Bolle, E., 163, 173, 201  
 Bonc, W. A., 129, 156, 186, 193, 195, 229,  
 290, 336, 370, 375, 410, 443  
 Bonhoeffer, K. F., 221, 229, 264, 315, 320,  
 323  
 Bonino, G., 553  
 Booy, J., 135  
 Boudouard, O., 131  
 Bowen, E. J., 387  
 Boyd, T. A., 443, 538, 554, 563  
 Bradford, B. W., 334, 356  
 Bradshaw, 38  
 Brenschede, W., 489  
 Breton, M. J., 178, 182  
 Brevoort, M. J., 240  
 Brewer, Keith A., 361  
 Briner, 401  
 Broeze, J. J., 514, 517, 539, 573, 583  
 Brooks, D. B., 544, 569  
 Brown, G. G., 525, 530  
 Brown, R. H., 290  
 Brown, W. E. J., 554  
 Broy, J., 135, 136  
 Brückner, H., 72  
 Brunner, 460, 462  
 Bunsen, R., 66  
 Bunte, K., 72, 121  
 Burgess, M. J., 131  
 Burgoyne, J. H., 469  
 Burke, S. P., 211, 377

- Bursian, 274  
 Bütetisch, H., 553  
 Calingaert, G., 567  
 Callendar, H. L., 461, 544, 569  
 Campbell, C., 20, 192  
 Campbell, H. C., 10, 189  
 Campbell, J. M., 142, 185, 536, 554  
 Carruthers, 380  
 Cassel, 46  
 Centnerszwer, 236  
 Chain, J. C., 370  
 Chamberlain, E. A. C., 421, 476  
 Chanova, J., 454  
 Chapman, D. L., 163  
 Chariton, J., 14, 284  
 Chaux, R., 462, 465, 544  
 Chesebro, 410  
 Chirkov, N., 306  
 Christiansen, J. A., 258, 380  
 Clark, A. L., 591  
 Clusius, K., 128, 290  
 Coates, 336  
 Cohen, E., 283  
 Cohen, L. L., 476  
 Coleman, J. D., 443, 540  
 Coslett, V. E., 333  
 Coward, H. F., 25, 35, 48, 97, 111  
 Cowen, L. G., 349, 466  
 Crew, 361  
 Crofts, 35, 39  
 Crussard, L., 107  
 Cunningham, J. P., 372  
 Dalton, 370  
 Dalton, R. H., 290  
 Damköhler, G., 118, 525, 529  
 Daniell, P. J., 107  
 Daniels, 481  
 David, W. T., 222, 238  
 Davies, 222  
 Davy, J., 25, 102, 284  
 Dawson, 481  
 Deacon, 290  
 Dinces, 396  
 Dixon, H. B., 35, 38, 161, 173, 180, 190, 197, 331, 437  
 Döbereiner, 290  
 Dommer, O., 72, 88, 113, 121  
 Donescu, M., 526  
 Driel, H. van, 514, 517, 539  
 Drinkwater J. W., 543  
 Drop, J., 135  
 Drugman, J., 422, 443  
 Dubowitzky, F., 303, 360  
 Duchêne, R., 515  
 Dufraisse, C., 135, 462, 544  
 Dumanois, P., 186, 190, 438, 443, 461, 570  
 Dumas, 284  
 Dupont, P., 466  
 Durgan, 396  
 Dussen, A. A. van der, 135  
 Dyck, W. J. D. van, 394, 497  
 Dykstra, F. J., 454, 485  
 Eberhard, 526  
 Echols, L. S., 398  
 Eckert, E., 239  
 Eckert, F., 485  
 Edgar, G., 454, 485  
 Egerton, A. C., 186, 190, 392, 398, 427, 432, 443, 462, 539, 548, 552, 567  
 Egloff, G., 442, 559  
 Egorow, 416  
 Eirchsen, C., 589  
 Elbe, G. v., 111, 119, 137, 145, 220, 238, 273, 297, 323, 344  
 Ellis, C., 93, 103, 388, 462, 467  
 Ellis, O. C. de C., 63, 92, 137, 143  
 Emeléus, H. J., 290  
 Emeléus, K. G., 47, 230, 234, 378  
 Emich, 35  
 Endres, W., 155  
 Engler, C., 380, 437  
 Erichsen, C., 232, 239  
 Ershov, 568  
 Estradère, S., 464, 515  
 Eucken, A., 108, 142, 175, 237  
 Evans, E. B., 554  
 Falk, 46  
 Faltings, K., 345, 490  
 Farkas, L., 20, 290, 304, 317, 374  
 Fedotova, 568  
 Fenning, 156  
 Féry, 221  
 Fichter, 390  
 Fiesel, 46  
 Finch, A., 192  
 Finch, G. J., 347, 349, 354, 356, 466, 476  
 Fiock, E. F., 68, 146  
 Flamm, L., 148  
 Fletcher, C. J., 416  
 Foord, S. G., 417, 485

- Förster, Th., 396  
 Fort, R., 378, 410, 468  
 Fourcroy, 283  
 Fowler, A., 231, 235, 290  
 Franck, J., 252  
 Frankenburger, W., 233, 317, 345, 374  
 Fraser, R. P., 178, 193, 195, 331, 375  
 Frewing, J. J., 398  
 Frey, 396  
 Freyer, 37, 46  
 Friauf, J. B., 173, 221  
 Friedel, 284  
 Frost, A. A., 295, 301, 320, 396  
 Fryling, C. F., 377  
 Fuchs, N., 576  
 Fugassi, P., 481  
 Fuhrmann, E. A., 592  
 Furness, W. C., 140  
  
 Gabler, 290  
 Ganter, W., 135  
 Gardner, J. B., 378, 410  
 Garner, W. E., 90, 238, 331, 342, 417, 554  
 Garstang, W. L., 303  
 Gates, S. F., 186, 190, 443, 465, 548  
 Gaudry, H., 90  
 Gautier, 46  
 Gaydon, 231  
 Geib, K. H., 261, 315, 372, 374  
 Gibson, C. H., 303  
 Giernet, 141  
 Gieszmann, W., 505, 536  
 Gill, F., 290, 437, 460  
 Gimmelman, G. A., 20, 419, 426  
 Giorgio, R., 400  
 Glockler, G., 591  
 Goldmann, F., 35, 39, 301, 321  
 Gomm, A. S., 331  
 Gorin, E., 374, 380  
 Görlacher, H., 289, 499  
 Gorschakov, G., 359  
 Gouy, 70, 87  
 Gradstein, S., 234  
 Grant, G. H., 300  
 Griffiths, E., 220, 223, 303  
 Griffiths, J. G. A., 418  
 Groth, W., 233, 319, 343, 490  
 Guenault, 232; 235  
 Guest, P. G., 25  
 Gunderley, G., 159  
 Gurian, D., 416  
 Gutschmidt, H., 128  
  
 Haber, F., 70, 85, 236, 291, 301, 303, 366, 374  
 Hadman, G., 302, 331, 335  
 Haffner, A. E., 405, 410  
 Hall, D. A., 238, 342, 372  
 Harris, E. J., 427, 432, 462  
 Harteck, P., 232, 290, 304, 319, 343, 374, 420  
 Hartel, v., 372  
 Hartmann, E., 72, 121, 375  
 Hartwell, F. J., 97  
 Harvey, F. E., 342  
 Hase, R., 224  
 Hatcher, W. H., 384, 390, 403  
 Häusser, F., 338  
 Hebl, L. E., 562  
 Hein, F., 470  
 Heiningen, J. van, 135  
 Heinze, R., 581  
 Heise, K., 462, 499, 548  
 Helier, 46  
 Helmore, W., 569, 580  
 Henning, F., 221  
 Henri, V., 234  
 Hepp, 396  
 Hermans, J. J., 135  
 Hershey, A. E., 223, 240, 526  
 Herzfeld, K. F., 251, 258  
 Hettner, G., 96  
 Hilferding, K., 263  
 Hill, D. A., 372,  
 Hill, S. G., 422  
 Hinschelwood, C. N., 20, 290, 294, 300, 302, 305, 310, 329, 378, 410, 468  
 van't Hoff, J. H., 1, 283  
 Hofmann, 554  
 Hofsász, M., 72, 89, 113  
 Holfelder, O., 574  
 Holm, J. M., 35, 48, 100  
 Holmes, M., 544  
 Hoogstraten, S. G. van, 437, 440, 539  
 Hopkinson, 137, 219  
 Horwood, J. F., 390, 463  
 Hottel, 526  
 Howes, D. A., 536, 539, 554  
 Howland, 384  
 Hsieh, M. S., 447, 482  
 Hubner, W. H., 442  
 Hugoniot, J., 167  
 Hulburt, 361  
  
 Ingle, H., 85, 236  
 Ivanov, K. I., 462

- Jahn, G.**, 72, 121  
**Janeway**, 542  
**Jentzsch, H.**, 485, 580  
**Jesse, H.**, 383  
**Johnson, C. H.**, 238, 341  
**Jones, G. W.**, 111, 131, 221  
**Jones, L. T.**, 489  
**Jordan, J.**, 222  
**Jordan, P.**, 252  
**Jorissen, W. P.**, 135, 284  
**Jost, W.**, 113, 175, 206, 263, 300, 312, 360, 433, 475, 511, 566  
**Joubert**, 284  
**Jouguet, E.**, 107, 140, 163  
**Jung, G.**, 263  
**Justi, E.**, 226
- Kane, G. P.**, 410, 476  
**Kannenber, 46**  
**Karde, K.**, 589  
**Kassel, L. S.**, 263, 273, 290, 292, 296, 300, 326  
**Kaveler, H. H.**, 222  
**Kearton, C. F.**, 290  
**Kelland, N. St.**, 20, 290  
**Khitrin, L.**, 69, 90  
**Killey, J.**, 443  
**Kimball, G.**, 263, 394  
**King, R. O.**, 569  
**Kirkbride**, 380  
**Kirkby, W. A.**, 63, 92, 103, 158  
**Kistiakowsky, G. B.**, 319, 390  
**Kitagawa, T.**, 229, 326  
**Klinkhardt, H.**, 317  
**Kluge, J.**, 145  
**Kneser, H.**, 142  
**Knudsen**, 96  
**Koelliker, E.**, 72, 79  
**Kohn, H.**, 219  
**Kokotschaschwili, V.**, 290  
**Kolodisew, Kh.**, 90  
**Kondratjew, V.**, 229, 234, 237, 290, 320, 339, 342  
**Kondratjewa, H.**, 237, 339, 342  
**Konen, H.**, 591  
**Kooyman, P. L.**, 437, 440, 539  
**Kopp**, 298, 331  
**Kopsch, U.**, 232, 290, 319, 372, 420  
**Kornfeld, G.**, 318, 319  
**Köttgen, H.**, 591  
**Kowalsky, A.**, 288, 298, 305, 331, 359  
**Krause**, 46  
**Kravetz, B.**, 306
- Krummenancher**, 390  
**Kühl, H.**, 240, 507  
**Kurlbaum, F.**, 221
- Labilladière, H. de**, 283  
**Ladenburg**, 284  
**Laffitte, P. F.**, 163, 178, 185, 188, 190, 290, 388, 443  
**La Fleur**, 135  
**Lake, F.**, 375  
**Lamont, F. G.**, 156, 229, 337  
**Landau, H. G.**, 31, 362  
**Lang**, 554  
**Langevin**, 362  
**Langweiler, H.**, 172, 188  
**Lauer**, 232  
**Lavin**, 317  
**Lavrov, F. (Lawrow, F.)**, 359  
**Lawrow, F. A.**, 416  
**Layng, T. E.**, 456  
**Leah, S.**, 222  
**Lean, B.**, 370  
**Le Braz, J.**, 135  
**Le Chatelier, H. L.**, 35, 92, 106, 131, 161, 177  
**Lees, C. H.**, 103  
**Le Floche**, 6, 35  
**Lehmann**, 263  
**Leicester, F. D.**, 290  
**Lenher, S.**, 390, 401  
**Levell, W. G.**, 554  
**Lewin, J.**, 466  
**Lewis, B.**, 111, 119, 137, 145, 173, 206, 220, 273, 297, 323, 344  
**Lewis, J. St.**, 438, 461, 568  
**Liefde, J. H. de**, 135  
**Liempt, J. A. M. van**, 235  
**Lind, S. C.**, 258  
**Lindeijer, E. W.**, 128, 135  
**Lindner, W.**, 585  
**Linkh, H. E.**, 145  
**Litterscheidt, W.**, 72  
**Littler, W. B.**, 142, 189  
**Livingstone, E. M.**, 290  
**Loomis, A. G.**, 220  
**Lorentzen, J.**, 499, 547  
**Lovell, W. G.**, 443, 538, 540, 554, 563  
**Ludlam, E. B.**, 288  
**Lunt, R. W.**, 47  
**Lütkemeyer, H.**, 259
- Mache, H.**, 65, 70, 80, 148  
**Macormac, M.**, 476

- Maesz, R., 392**  
**Magat, M., 143, 238**  
**Mahler, E. A., 350**  
**Malinowski, A. E., 366**  
**Mallard, E., 35, 39, 92, 106, 161, 177**  
**Mandlekar, M. R., 191, 476**  
**Marder, M., 581**  
**Mardles, E. W. J., 290, 437, 460, 46**  
**Marek, 396**  
**Marshall, A. L., 317**  
**Marum, van, 283**  
**Marvin, C. F., 68, 146**  
**Mason, W., 27**  
**Mathes, E., 591**  
**Matla, W. P. M., 135**  
**Maxwell, G. B., 142, 547**  
**Mayer-Schuchard, C., 165**  
**McAlevy, 409**  
**McCluer, 396**  
**McDavid, 35**  
**McDonald, R. D., 401, 403**  
**Meek, C. A., 47**  
**Meiter, E. G., 48, 57**  
**Melville, H. W., 288, 290**  
**Mesée, H. J., 470**  
**Meyer, 46**  
**Michelson, 70, 107**  
**Midgley, T., 443, 502, 519, 545**  
**Milas, 460**  
**Milner, 406**  
**Mitscherlich, 46**  
**Mittasch, A., 292**  
**Moelwyn-Hughes, 294, 310, 330**  
**Mole, G., 360, 362, 569**  
**Mondain-Monval, P., 400, 438, 442, 461**  
**Moore, 35**  
**Morgan, E., 137**  
**Morgan, J. D., 56, 60**  
**Morikawa, K., 372**  
**Morton, 396**  
**Moss, H., 569**  
**Moureu, C., 381, 462, 544**  
**Mücke, 142**  
**Müffling, L. v., 32, 113, 279, 300, 360, 392, 433, 566**  
**Muir, J. J., 290**  
**Müller, G., 72**  
**Müller, R., 586**  
**Müller-Hillebrand, D., 101, 593**  
**Münch, 46**  
**Munro, 427, 447**  
**Musgrave, F. F., 336**  
**Nagai, 135**  
**Nägel, A., 159, 574**  
**Nalbandjan, A., 297, 303, 360**  
**Nash, A. W., 536, 539**  
**Natta, G., 553**  
**Neugebauer, F., 553**  
**Neumann, K., 239, 290, 579, 588**  
**Neumann, M. B., 20, 416, 444, 453, 464**  
**Newitt, D. M., 129, 156, 186, 331, 336, 378, 415, 436, 469, 472**  
**Nielsen, 513**  
**Norrish, R. G. W., 278, 290, 303, 380, 404, 417, 426, 485**  
**Nusselt, W., 107**  
**Oettingen, v., 141**  
**Ohlmer, 334**  
**Oidenberg, O., 306, 320**  
**Onkiehong, B. L., 135**  
**Ootuka, H., 236**  
**Oppenheimer, F., 303**  
**Outridge, L. E., 156, 337**  
**Parker, 102**  
**Parkinson, R. M., 238**  
**Passauer, 72**  
**Pařat, F., 380**  
**Paton, R. F., 223**  
**Patrie, M., 178**  
**Paul, 396**  
**Payman, W., 107, 140, 174, 177, 188**  
**Pearse, R. W., 230**  
**Pearson, T. G., 320**  
**Pease, R. N., 302, 310, 386, 396, 398, 427**  
**Peletier, L. A., 437, 440, 514, 517, 539**  
**Perkin, W. H., 378, 437**  
**Perrot, G. St. J., 220**  
**Peters, G., 135**  
**Petrikaln, 236**  
**Philippovich, v., 502, 513, 531**  
**Philipps, N. W. F., 372**  
**Pichler, H., 414**  
**Pickering, S. F., 85**  
**Pickles, 305**  
**Pidgeon, L. M., 398, 444, 543, 552, 569**  
**Pier, M., 145, 553, 582**  
**Pignot, A., 443**  
**Pigulevskii, V. V., 388, 467**  
**Plentz, 130**  
**Plewes, A. C., 405**  
**Polanyi, M., 236, 258, 372**  
**Polland, F. H., 342**



- Polly, O. L., 467  
 Pope, J. C., 454  
 Posthumus, K., 135  
 Predvoditelev, A., 83  
 Prettre, M., 35, 39, 290, 310, 314, 331, 378, 429, 439, 442, 454  
 Price, T. W., 35, 442  
 Prior, A. M., 356  
 Puddington, 396  
 Pugh, A., 90  
 Pye, D. R., 38, 452, 472, 572  
  
 Quanquin, 400, 442  
  
 Rabinowitsch, E., 263  
 Rance, 405  
 Rassweiler, G. M., 239, 514, 525, 551  
 Reder, R., 414  
 Reichard, 264  
 Reichardt, H., 323  
 Reicher, 284  
 Rendel, T. B., 562  
 Rhead, 102  
 Ribaud, G., 90  
 Riblett, E. W., 422  
 Ricardo, H. R., 506, 507, 554, 573  
 Rice, F. O., 394  
 Rice, K. K., 395  
 Rice, O. K., 10, 467  
 Richardt, F., 70, 236  
 Rideal, E. K., 290, 462  
 Rieche, A., 406, 442  
 Rieke, F. F., 320  
 Riemann, B., 167  
 Riesenfeld, E. H., 416  
 Ritchie, A., 290  
 Rjabinin, 290  
 Robinson, H., 93, 140, 178  
 Roffey, F., 238, 342  
 Rohrmann, W., 433  
 Rolfe, A. C., 310, 330  
 Rollefson, G. K., 416  
 Rosenberg, S., 384  
 Rosenblum, 372  
 Rothrock, 516, 523, 589  
 Roxburgh, H. L., 290  
 Rummel, K., 210, 217  
 Rumpf, K., 236, 287  
  
 Sally, 317  
 Schack, A., 238  
 Schaefer, D., 575, 580  
 Schay, G., 236  
 Schenk, P. W., 317  
 Schmidt, A., 206  
 Schmidt, A. W., 554  
 Schmidt, E., 501, 525  
 Schmidt, F. A. F., 534, 587  
 Schmidt, H., 219, 223  
 Schmidt, O., 396  
 Schnauffer, K., 63, 506, 527  
 Schneider, P., 581  
 Schottky, W., 253  
 Schou, S. A., 234  
 Schulte, F., 575  
 Schultze, G., 221  
 Schulze, G., 372  
 Schulze, H., 143, 532  
 Schumacher, H. J., 242, 418, 489  
 Schumann, T. E. W., 211, 377  
 Schuster, A., 173  
 Schweitzer, P. H., 577  
 Seeber, F., 591  
 Seiler, E., 365  
 Selden, 589  
 Semenoff, N., 6, 270, 274, 284, 290, 297, 303, 331, 360, 421, 448  
 Semenowa, N., 295  
 Serbinow, A., 416  
 Serruys, M., 531, 534, 570  
 Seuffert, G., 121  
 Shepherd, W. C. F., 140, 177, 188  
 Shtsholkin, K., 190, 523  
 Silver, R. S., 29  
 Sloane, R. W., 365  
 Slotin, L., 379, 410  
 Smallwood, 316  
 Smith, D. F., 406  
 Smith, E. C. W., 47  
 Smith, F. A., 74, 83, 85  
 Smith, F. L., 539, 547  
 Smith, H. A., 319  
 Smithells, A., 85, 236, 437  
 Smits, 409  
 Smittenberg, J., 437, 440, 539  
 Smoluchowski, M. v., 285  
 Snowdon, F. F., 379  
 Sokolik, A., 190, 306, 520, 523  
 Sokov, P., 419, 426  
 Sommers, H. S., 306  
 Sorokin, 274

- Spence, R., 379, 404, 489  
 Spencer, 516, 523  
 Sprake, C. H., 554  
 Stadt, J. v. d., 284  
 Stansfield, R., 591  
 Staudinger, H., 381  
 Steacie, E. W. R., 21, 372, 384, 396, 403  
 Steiner, W., 263, 316  
 Stephens, H. N., 470  
 Stern, O., 340  
 Stern, W., 306  
 Stevens, F. W., 67, 90  
 Storch, H. H., 273, 296, 300, 326, 396  
 Stuurmann, 409  
 Style, D. W. G., 379, 463  
 Sutton, R. W., 347, 356  
  
 Taffanel, 6, 35  
 Tauss, J., 289, 575  
 Tauzin, P., 299, 306, 453  
 Tawada, 238  
 Taylor, H. A., 290  
 Taylor, H. S., 304, 312, 317, 372, 545, 567  
 Taylor-Jones, E., 56, 347  
 Teclu, N., 85, 236  
 Teichmann, H., 475, 511  
 Terres, 111, 130  
 Tett, H. C., 290, 437, 460  
 Thee, W. C., 591  
 Theis, E., 292  
 Thompson, H. H., 302, 476  
 Thompson, H. W., 20, 290, 303, 331, 398  
 Thornes, 480  
 Thornton, W. M., 346  
 Tietz, E. L., 387  
 Tingwaldt, C., 221  
 Titman, H., 140  
 Tizard, H. T., 35, 452, 472, 502  
 Todes, O. M., 14  
 Townend, D. T. A., 129, 156, 186, 191,  
     290, 336, 370, 410, 421, 447, 472  
 Trautz, M., 290  
 Trenner, N. R., 372  
 Tschirkow, N., 416  
 Turpin, G. S., 437  
 Tutakin, P. M., 453, 464  
  
 Ubbelohde, A. R., 234, 392, 488, 543, 551  
 Ubbelohde, L., 72, 79, 89, 113, 121, 382  
  
 Vaidya, W. M., 233, 235, 290  
 Vieille, P., 161  
  
 Vogt, K., 366  
 Voinov, A., 520  
 Volmer, M., 340  
 Vriend, J. A. de, 235  
  
 Wal, M. J., van der, 135  
 Wallace, J., 410, 418, 485  
 Walls, J., 174  
 Walta, 284  
 Walter, B., 348  
 Wartenberg, H. v., 46, 372  
 Watkins, G. B., 519  
 Watson, 290  
 Weiszberg, J., 380  
 Weiszweiler, A., 188  
 Wellard, 461  
 Wendlandt, R., 178  
 Wentzel, W., 576  
 Werner, G., 130  
 Weston, F. R., 231, 331, 342  
 Wheeler, R. V., 28, 56, 137, 158, 348  
 Wheeler, T. S., 405  
 Wheeler, W. H., 193  
 White, A. G., 104, 378, 442, 482  
 Whitworth, C., 142, 189  
 Wietzel, G., 367, 456  
 Wild, 380  
 Wilken-Jordan, T. J., 591  
 Williamson, A. T., 300, 305, 311, 329  
 Wilson, H. A., 366  
 Wilson, R. E., 443, 519  
 Winnacker, K., 462, 466, 499, 548  
 Winter, 391  
 Withe, 35  
 Withrow, C. L., 239, 514, 525, 542, 551  
 Wohl, K., 143, 145, 238  
 Wolfenden, J. H., 301  
 Wolfer, H. H., 587  
 Wolfhard, H. G., 224  
 Wood, W. C., 263  
 Woodhead, D. W., 177, 192  
 Wunenburger, 401  
  
 Youker, M. A., 456  
 Yumoto, K., 355  
  
 Zeise, H., 226, 228, 323  
 Zerbe, C., 485  
 Zherko, 396  
 Zinner, K., 571, 575, 590  
 Zisch, K., 236  
 Ziskin, M., 229, 320



# SUBJECT INDEX

## A

- Absorption spectra of organic compounds, 398-400
- Acetaldehyde, 408, 422, 425, 429, 430, 436, 441, 451, 467, 478, 545
  - absorption spectrum, 399
  - auto-ignition at higher pressures, 480
  - disintegration, 397
- Acetaldehyde oxidation, cold flames, 388, 441
  - induction period, 383
  - influence of wall, 383, 384
  - inhibition by additions, 382, 387
  - photochemical reaction, 387
  - reaction mechanism, 382-385
  - reaction products, 381, 386
  - velocity law, 380
- Acetone, 495, 546
  - auto-ignition at higher pressures, 481
  - disintegration, 396
  - ignition temperature, 43, 481
  - maximum combustion velocity in mixture with air, 122
- Acetophenone, 480
- Acetyl peroxide, 434, 544, 545, 546
- Acetylene, ignition limits in air and oxygen, 110, 132
  - influence of, on the combustion velocity of oxygen-hydrogen, 374
  - maximum combustion velocity in mixture with air, 122
  - oxygen mixtures, detonation pressures, 189
  - oxygen- (air-) mixtures, detonation limits, 184
  - oxygen- (nitrogen-) mixtures, detonation velocity, 179, 181
  - oxygen welding burner, temperature measurement, 223
  - reaction with atomic hydrogen and oxygen, 370
- Acetylene, knocking behavior, 556, 561
- Acetylene hydrocarbons, critical compression ratios, 556
- Acetylene oxidation, influence of nitric oxide additions, 406
  - reaction mechanism, 404
  - reaction products, 369, 389, 400-404
  - reaction velocity, 403
  - surface influence, 402, 403
- Acids, organic (*see* specific substances, oxidation products)
- Activation, apparent heat of, in ignition
  - by hot pellets, 31
  - compound reactions, 264
  - heat of, and heat production, 258
  - heat of atom and radical reactions, 261, 262, 316-322
- Active particles in the detonation wave, 175
  - destruction in the gas phase, 391
  - diffusion in the burning zone, 116
  - production of, 315
  - reactions, 314-322
- Acyl peroxide, 545
- Adsorption, 264, 310-314
- Adsorption layer, influence of, in chain explosions, 291, 311-315
- After-burning, 137
- Afterglow in engines, 239
- Alcohol, influence of, on acetaldehyde oxidation, 387
- Alcohol oxidation, luminescence and cold flames, 234, 437, 441
- Alcohols, knocking behavior, 560
  - oxidation stability, 456
  - reaction products in hydrocarbon combustion, 367
- Aldehyde oxidation, 378-392
  - in the liquid phase, 380*ff.*
  - luminescence and cold flames, 234, 437*ff.*
  - negative catalysis, 380
  - spectroscopic observation, 391
  - wall influence, 391

- Aldehyde radicals, 492  
 Aldehydes, 433, 464, 466, 467, 477  
   auto-oxidation, 380*ff.*  
     intermediary products in engine combustion, 542-554  
     reaction products in hydrocarbon combustion, 368  
 Alkyl hydroperoxide, 545  
 Alkylidene peroxide, 546  
 Alkylidene peroxide, 545-547  
 Ammonia, 454  
   influence of, on carbon monoxide combustion, 305  
 Ammonia-oxygen mixtures, detonation limits, 184  
   ignition limits in air, 132  
   ignition range of the system  $\text{NH}_3\text{-H}_2\text{-O}_2$ , 134, 135  
   sensitizer of the light reaction of oxygen-hydrogen, 305  
 Amyl alcohol, 441, 560  
 Amyl benzol, 558  
 Amyl cyclohexane, 557  
 Amyl cyclopentane, 557  
 Amyl nitrite, 544, 546  
 Amylene, 478, 547  
 Amylene peroxide, 545  
 Angle measurement in the Bunsen flame, 86  
 Aniline, influence of, on slow oxidation and knocking, 367, 383, 549, 567  
 Aniline equivalents, 565, 566, 581  
 Anti-knocks, 351, 442, 443, 465, 496, 497, 499, 538, 547-550, 557, 560, 567-570  
   chemical structure, 553-567  
   influence, of the degree of distribution, 548  
     on hydrocarbon oxidation, 45, 496  
     on luminescence, 442, 443  
     on normal combustion velocity, 122, 123  
     on slow oxidation, 568  
   (See also specific substances)  
 Argon, influence of, on oxygen-hydrogen combustion, 37*ff.*, 296, 298, 299  
   on carbon monoxide combustion, 334  
 Aromatic hydrocarbons, knocking behavior, 558, 561  
   oxidation, 467-469  
 Atoms, concentrations of, in the dissociation equilibrium, 315, 323  
   in oxygen-hydrogen combustion, 321-325  
   free, reactions of, 314-321, 392  
   reactionability, 259  
 Aureoles, 237  
 Auto-catalysis, 281, 308, 367  
 Auto-diffusion, 250  
 Auto-ignition, and cold flames, 477-487  
   definition of, 1, 4*ff.*  
   in the Otto engine by overheated cylinder spots, 533  
   (See also Ignition temperature)  
 Autoxidation, 380*ff.*  
 Autoxidator, 381  
 Azomethane, disintegration and explosion, 10
- B**
- Batswing burner in industrial firing, 215-218  
 Benzaldehyde, 380, 467, 470  
 Benzoic acid, 470  
 Benzol, 461, 463, 465  
   absorption spectrum, 399  
   auto-ignition at higher pressures, 475, 487  
   disintegration constant, 396  
   ignition limits in air, 132  
   knocking behavior, 525, 538, 546, 558, 564, 567  
   maximum combustion velocity in mixture with air, 122  
   oxygen mixture, detonation velocity, 179  
   reaction with atomic hydrogen and oxygen, 372  
 Benzol hydrocarbons, oxidation, luminescence and cold flames, 438, 440  
 Benzol oxidation, course of reaction, 466-469  
   induction period, 467  
   reaction products, 467  
 Benzyl acetylene, 558  
 Benzyl alcohol, 470  
 Benzyl radicals, 471  
 Black body, emission capacity, 235  
 Boltzmann factor, 254  
 Bomb explosions, 136-159, 238  
 Bond energies, 395

- Branching probability in chain reactions,
- Breaking of the gas flow in the Bunsen flame, 79-80
- Breaking probability in reactions with chain branching, 268*ff.*
- Bromine, and hydrogen reaction, kinetics, 258-264  
influence of, on oxygen-hydrogen combustion, 303
- Bunsen burner, 69, 70, 223  
composition of the intermediate gas, 236, 237
- Bunsen flame, color, 233  
influence of secondary air, 236  
temperature measurement, 223  
tip of, 75-77, 85, 127
- Bunsen method for measuring combustion velocity, 66
- Burner dimensions, influence of, on the height of a diffusion flame, 213
- Burning surface, 65  
in the Bunsen flame, 74-89  
in tubes, 93*ff.*
- Burning zone, 76  
in diffusion flames, 211  
propagation with ordinary flame and in detonation, 172  
structure, 106-108, 115-120, 134  
temperature distribution, 107, 108  
temperature measurement, 222  
thickness, 108, 109
- Butane (and isomeres), auto-ignition  
at higher pressures, 475-478  
disintegration constant, 396  
knocking behavior, 559  
oxygen-mixtures, detonation limits, 184  
oxygen- (nitrogen-) mixtures, detonation velocity, 179
- Butane oxidation, induction periods, 450-452
- Butanol, 559  
disintegration, 396
- Butyl-amyl ether, 559
- Butyl benzol, 558
- isom.-Butyl-butyl ether, 559
- Butyl cyclohexane, 557
- Butylene, 478
- Butyraldehyde, 441, 442  
absorption spectrum, 399
- Butyraldehyde oxidation, gross reactions, 456  
intermediate products, 456
- Butyraldehyde peroxide, 546
- C
- Cadmium, 548
- Camera for measuring detonation velocities, 178
- Candle flame, 209
- Capacity components in spark ignition, 346, 355-356
- C<sub>2</sub>-radical in hydrocarbon combustion, 367  
spectrum, 231-234
- Carbon dioxide, influence of, on carbon monoxide combustion, 334  
on ignition temperatures, 37*ff.*
- Carbon disulphide, maximum combustion velocity in mixture with air, 122
- Carbon disulphide flame, spectrum, 235
- Carbon disulphide oxidation, cold flames and luminescence, 235, 239, 437  
explosion limits, 290
- Carbon disulphide-oxygen mixture, auto-ignition at higher pressures, 473, 474  
detonation velocity, 179  
ignition limits in air, 132  
ignition temperature, 43  
oxygen-(nitric oxide)-mixtures, reaction, 162
- Carbon monoxide-air mixture, combustion velocity with, air-(oxygen-) mixtures, 68, 122  
ignition temperatures, 40*ff.*, 332-335  
hydrogen-oxygen-(air)-mixtures, detonation limits, 182, 183  
oxygen flame, spectrum, 231  
oxygen mixture, detonation, 179, 180, 200  
oxygen-(air)-mixtures, flame temperature, 223  
varying H<sub>2</sub>O content, 121  
ignition limits in air and oxygen, 110, 129-132
- Carbon monoxide combustion, catalytic reaction, 333  
dependence on antecedents, 334  
in electrical discharges, 349*ff.*

- Carbon monoxide combustion, explosion limits, 331-334  
 ignition of the dry mixture, 331  
 influence of, dimension of the container, 333  
 foreign gas additions, 334  
 mixture composition on the explosion limits, 332  
 water vapor addition, 121, 238, 331*ff.*  
 luminescence, 237, 238, 437  
 mechanism, 342  
 NO-formation, 337-339  
 reaction outside the explosion limits, 334  
 rise in pressure, 157, 158  
 spectroscopic investigation, 336-342
- Carbonic acid, absorption bands, 230, 231, 336
- Catalysis in oxygen-hydrogen reaction, 292, 308  
 in ignition by heated surfaces, 22, 25  
 negative, 380
- Catalytic oxidation of hydrocarbons, 367
- Cathode material, influence of, on conversion in electrical discharges, 349*ff.*
- Cetane, 582
- Cetene, 568, 580-584, 586
- Cetene number, 580-584, 586
- CFR engine, 536
- CFR-engine process for fuel testing, 536
- CFR-research method for fuel testing, 536
- Chain branching, 264-281  
 in the gas phase, 276  
 influence of pressure, 269, 270  
 reaction order, 277, 279, 281, 327  
 at the wall, 276
- Chain breaking, 259, 266*ff.*  
 in the gas phase, 271-280, 289, 291  
 reaction order, 277, 279, 281, 327, 328  
 at the wall, 269-280, 285
- Chain explosion, boundary conditions, 267, 268  
 development in time, 281-283  
 examples, 283-291  
 formal relations, 266-268  
 (See also specific substances)
- Chain induction, 259  
 at the wall, 291
- Chain reactions, 258-291  
 in non-thermal spark ignition, 364
- Chain scheme and reaction equation, 261, 262
- Chain thermal explosion, 271, 283
- Chemiluminescence, 219, 229, 235-241, 324, 336  
 light yield, 239
- Chlorine, hydrogen mixtures, pressure rise in bomb explosions, 188  
 ignition range of the system,  $H_2$ -NO- $Cl_2$ , 134  
 influence of on oxygen-hydrogen combustion, 303
- Chlorine-monoxide, disintegration and explosion, 20
- Chlorine-oxygen-hydrogen explosion, 290, 317
- CH-radical in hydrocarbon combustion, 367  
 spectrum, 231-233
- Chrono-electrical recording of flame movements, 161
- Coal dust, thermal explosion, 14
- Coal tar oil, 571, 577, 590
- Cold flames, pressure and temperature, 444, 445  
 and auto-ignition, 475-485  
 and chain reactions, 453, 454  
 critical pressure limits, 447-448  
 in the engine, 437, 441  
 of hydrocarbon-air-(oxygen-)mixtures, 234  
 in hydrocarbon combustion, 368, 378, 437-471  
 of hydrocarbons, spectrum, 230, 234  
 with hydrogen- or oxygen-atoms, 231  
 induction periods, 449-453  
 and luminescence, 235, 437-471  
 transition to explosion, 451-453  
 velocity, 439, 482
- Combustion, definition, 1
- Combustion velocity (see Normal combustion velocity)
- Combustion velocity and compression ratio in the Otto engine, 505
- Composition limits, 13
- Compression ratio, critical, 538, 556-559
- Compression ratio and combustion velocity in the Otto engine, 505

- Constant pressure bomb, 65-68  
Constant volume process, 572, 573  
Convection, influence of on ignition limits, 128  
Cooling in engine combustion, 526  
Crude oils, 583  
Cyanogen-oxygen-(nitrogen-)mixtures, detonation velocity, 180  
Cyclical hydrocarbons (*see* specific substances)  
Cyclical-process temperatures for the Otto engine, 503  
Cyclohexadiene, 465, 558  
Cyclohexane, disintegration constant, 397  
    ignition limits in air, 132  
    maximum combustion velocity in mixture with air, 122  
    oxidation and knocking behavior, 462, 465, 466, 475, 507, 537, 547, 557, 563  
Cyclohexene, 439, 465, 558  
Cyclopentadiene, 558  
Cyclopentane, 557  
Cyclopentene, 558  
Cyclopropane, ignition limits in air and oxygen, 111, 132  
Cymol (methyl-*i*-propylbenzol), 558
- D
- Davy's safety lamp, 102  
Deactivation, 259*ff.*, 271*ff.*, 291  
Decahydronaphthalene, 557  
Decane, 462  
Dehydration of hydrocarbons by H- and D-atoms, 372  
Detonation, 64, 159-209  
    beginning of, 160-162, 196  
    flame path up to beginning, 186, 187  
    influence of, additions, 176, 177, 179, 180, 190-192  
    the change in diameter of the tube, 185, 186  
    external factors, 185-188  
    and knocking process, 517-521  
    origin, 197, 199  
    and reaction velocity, 172, 173, 174, 179-181, 207-209  
    static, 170  
    theory, 163-173, 201-209  
Detonation limits, 173, 182-185  
    measurement, 178  
Detonation photographs, 162, 193-198, 200, 207  
Detonation pressures, 188-189  
    during the origin of a detonation wave, 189  
Detonation velocity, experimental determination of, 173-182  
    influence, of the pressure, 187  
    of the temperature, 186  
    numerical values, 174, 177, 179, 180, 181  
Detonation wave, 164*ff.*  
    energy supply, 208  
    coupling with combustion, 199, 207-209  
    reaction in the front, 207-208  
    stability, 204-211  
Deuterium, combustion, 301  
Deuterium atom, reaction with hydrocarbons, 373  
Diacetyl, absorption spectrum, 399  
Diacetyl peroxide, 387  
Dialkyl monohydroxyperoxide, 545  
Dialkyl peroxide, 545  
Dibenzyl, 470  
Dibutyl ether, 442, 559  
Dicyclopentadiene, 558, 563  
Diesel combustion, heterogeneous reaction, 583  
    spectra, 233, 589  
Diesel engine, 430, 571-590  
    after-burning, 580, 589  
    demands on the fuel, 571  
    diffusion processes, 576  
    heterogeneous reaction in combustion, 583  
    injection process, 574-576  
    knocking, 571  
    mixture formation, 574, 575, 588  
    reaction kinetics of the ignition process, 583-588  
    course of combustion, 573-580  
    evaporation of droplets, 575-577, 589  
    ignition delay, 571, 578*ff.*  
    ignition of isolated droplets, 585  
    ignition process, 572-590  
    working method, 572-573  
Diesel fuels, determining ignitibility, 580-583  
Diesel indices, 581  
Diethyl benzol, 558



Diethyl cyclohexane, 557  
 Diethyl ether, combustion velocity in mixture with air, 122  
   detonation, 184  
   disintegration, 398  
   ignition limits in air and oxygen, 110, 132, 482  
   ignition temperature, 45, 481  
   oxidation, 442, 465, 473, 479-481  
 Diethyl hexane, 555  
 Diethyl peroxide, 462-464, 545, 546  
 Diethyl selenide, 567  
 Diethyl telluride, 567  
 Diethylamine, 383  
 Diffusion of active particles, 117  
   in the Bunsen flame, 76, 84  
   in the burning zone, 115-117  
   in combustion in tubes, 98  
   in flame propagation, 105ff.  
   in flames of non-premixed gases, 210-218  
   in ignition by heated surfaces, 24, 32  
   influence in reactions with chain branching, 269-280, 309  
   kinetic theory, 249  
   in spark ignition, 47, 48, 364  
 Diffusion flames, 210-213  
 Dihydroxy-alkyl peroxide, 545  
 Dihydroxy-ethyl benzol, 469  
 Di-isobutylene, 466  
   disintegration constant, 396  
 Diisopropyl ether, 442, 559  
   auto-ignition at higher pressures, 483  
 Dimethyl butadiene, 555  
 Dimethyl butane, disintegration constants, 396  
 Dimethyl cetene, absorption spectrum, 399  
 Dimethyl cyclohexane, 557  
 Dimethyl cyclopentane, 557  
 Dimethyl fulvene, 558  
 Dimethyl hexane, 457, 498  
 Dimethyl octane, 555  
 Dimethyl pentane, 555  
 Dimethyl pentene, 555  
 Diolefins, 555  
 Dioxymethyl peroxide, 407, 434  
 Dipentene, 558  
 Diphenyl, formation in sooty flames, 232  
 Diphenylamine, 383  
 Discharges in explosive mixtures, 348-364

Discharges in explosives, spectroscopic observations, 354, 355  
 Disintegration constants of paraffins, 396  
 Dispersion of sound velocity, 175  
 Dissociation, degrees of, in case of  $H_2$ ,  $O_2$ ,  $H_2O$ , 323  
   influence of, on efficiency of Otto engine, 502, 507  
   on flame temperatures, 224  
   on knocking tendency, 534  
 Divinylether, ignition limits in air and oxygen, 111, 132  
 Dodecane, 465  
 Double bond, influence of on reactivity, 439  
 Double bond rule, 395  
 Double impact associations of organic radicals, 393  
 Dynamic method for measuring combustion velocity (*see* Gouy's method)

## E

Efficiency and compression ratio in the Otto engine, 500-505  
 Efficiency of the Otto engine with knocking combustion, 528-532, 540  
 Electrical fields, influence of, on detonation, 201  
   on flame propagation, 364  
 Emission and absorption ability, determining flame temperatures, 222, 223, 235  
 Energy chains, 268  
   in carbon monoxide combustion, 342, 343  
 Energy distribution, 251ff.  
   distribution function for gases, 254, 255  
 Energy exchange between vibration and translation movement, importance of, for detonation, 175  
 Engine, cold flames, 435, 439  
   combustion, 240  
   heat conduction, 240, 534-536  
   maximum temperature, 240  
   radiation and temperature, 239-241  
   spark ignition, 360, 361  
   temperature measurement, 240  
   turbulence, 240, 506  
   (*See also* Otto engine and Diesel engine)

- Engine combustion, absorption and emission spectra, 542-544**  
catalytic reactions, 542
- Entropy in the stable detonation wave, 203, 204**
- Equilibrium constants of dissociation reactions, 322**  
and reaction velocity, 257, 258
- Ethane, auto-ignition at higher pressures, 480, 484, 485**  
disintegration constants, 396  
ignition limits in air and oxygen, 110, 132  
knock behavior, 555, 559  
oxygen mixture, detonation velocity, 179  
reaction with atomic hydrogen, 372
- Ethane oxidation, explosion limits, 425**  
induction period, 424ff.  
influence of additions, 21, 424, 426, 427  
intermediary products, 425  
methanol and ethanol formation, 377  
reaction mechanism, 426, 427  
reaction products, 370, 424-425  
reaction velocity, 423-425  
wall influence, 424, 425
- Ethanol, 422, 424, 432, 466, 485**  
auto-ignition at higher pressures, 485  
formation in ethane oxidation, 377  
ignition limits in air, 132  
ignition temperature, 43, 441, 485  
knocking behavior, 546, 560, 567  
luminescence, 440  
oxygen-(nitrogen-)mixtures, detonation velocity, 179
- Ether, 473, 474**  
knocking behavior, 559
- Ether oxidation, luminescence and cold flames, 230, 234, 436ff.**
- Ethyl azide, disintegration and explosion, 10, 19**
- Ethyl benzol, 468-470, 549**
- Ethyl cyclohexane, 557**
- Ethyl cyclopentane, 557**
- Ethyl ether, 441, 473**  
maximum combustion velocity in mixture with air, 122  
ignition limits in air and oxygen, 111, 481
- Ethyl fluid, 443, 540, 567**
- Ethyl gasoline, 547**
- Ethyl hexane, 457**
- Ethyl iodide, 387, 489, 549, 567**
- Ethyl pentane, 555**
- Ethyl pentene, 555**
- Ethyl propionate, 390**
- Ethylene, 289, 290, 425**  
absorption spectrum, 399  
auto-ignition at higher pressures, 487  
ignition limits in air and oxygen, 111, 132  
knocking behavior, 555  
maximum combustion velocity in mixture with air, 122  
oxygen mixtures, detonation pressures, 189  
temperature influence on detonation, 186  
oxygen-(nitrogen-)mixtures, detonation velocity, 179, 181  
reaction with atomic hydrogen, 372
- Ethylene bromide, 443, 567**
- Ethylene dibromide, 540**
- Ethylene flame, spectrum, 233**
- Ethylene glycol, 406**
- Ethylene oxidation, induction period, 408, 409**  
influence of foreign gas additions, 406, 409  
intermediary products, 408-409  
luminescence, 440  
reaction mechanism, 409, 410  
reaction products, 370, 406, 408  
reaction velocity, 408, 409  
wall influence, 406
- Ethylene oxide, 406, 408, 409**  
ignition limits in air, 132  
ignition range of the system ethylene-oxide-air-CO<sub>2</sub>, 135
- Ethyl-isopropyl ether, 559**
- Ethyl-sec.-butyl-ether, 559**
- Ethyl-tert.-amylether, 559**
- Ethyl-tert.-butyl-ether, 559**
- Exchange reaction, 373**
- Exhaust gases, path in detonation, 205**  
velocity, 160
- Experimental engine for flame pictures, 515**
- Explosion, adiabatic and almost adiabatic, 18**  
in closed containers, 136-159  
compression effects, 138  
cooling curve, 139  
flame pictures, 139, 140

- Explosion, in closed containers, gas vibrations**, 142, 143, 144, 159  
     **pressure recording**, 142, 144*ff.*  
     **pressure rise**, 149*ff.*  
     **schlieren photographs**, 140, 142  
     **temperature drop in the burned gas**, 137, 138, 149*ff.*  
     **theory**, 136  
     **conditions for, in reactions with chain branching**, 266*ff.*  
     **generalized according to Semenov**, 16  
     **definition of**, 280  
     **degenerate**, 405, 428  
     **at high initial pressure**, 157, 158  
     **influence of foreign gas additions**, 270*ff.*  
     **in open containers**, 90–106  
     **propagation**, 60, 135  
     **reaction and heating velocity**, 15  
     **in reaction of the "zero order,"** 15  
     **suppression**, 14, 133  
     **as a thermal phenomenon**, 3  
**Explosion-endangered industries, use of electrical equipment**, 99  
**Explosion equations**, 14*ff.*  
**Explosion limits, definition of**, 7, 12–13  
     **methods of determining**, 293, 331, 333  
     **in reactions with chain branching**, 269–280  
     (*See also* Ignition temperature and Explosion pressure)  
**Explosion pressure, critical**, 7  
     **in reactions with chain branching**, 274  
**Explosion prevention**, 133
- F**
- Farnboro indicator**, 530, 531  
**Fatty acids**, 437*f.*, 456  
**Firedamp**, 25, 56*ff.*  
**Flame, definition of**, 60  
**Flame form in diffusion flames**, 210–211  
**Flame front, form**, 94  
     **and percussion wave**, 198  
     (*See also* Burning zone)  
**Flame height in diffusion flames**, 213, 214  
**Flame penetration, prevention of**, 102, 103  
**Flame propagation**, 62*ff.*  
     **in chronoelectrical recording**, 161  
     **in closed containers**, 136–145  
     **heat conduction**, 125–126  
     **Flame propagation, overlapping of vibrations**, 93, 103–106, 161, 162  
     **photographic recording**, 65–68, 91*ff.*, 161*ff.*  
     **stability**, 103, 106  
     **theory**, 106–120  
     **uniform**, 92  
     **Flame-splitting tube**, 84, 85, 236  
**Flame temperatures**, 219–241  
     **computation**, 225–228  
     **example of**, 226–228  
     **measurement**, 218–224  
**Flame velocity**, 62*ff.*, 160*ff.*  
     **and bending the burning surface**, 126, 127  
     **dependence on wall material**, 100–103  
     **effect of gravity**, 94  
     **influence of, narrowing the tube**, 158  
     **and normal combustion velocity**, 62  
     **in the Otto engine**, 506  
     **and pressure rise**, 145*ff.*  
     **in tubes**, 91*ff.*  
**Flames of non-premixed gases**, 62, 210–218  
     **experiments on models**, 216  
     **flow conditions**, 214–218  
     **mixing process**, 214–227  
     **Flow processes** (*see* Gas flow)  
**Formaldehyde**, 396, 406, 411, 416*ff.*, 422, 429, 434, 436, 437, 543, 551  
     **absorption spectrum**, 234, 399  
     **auto-ignition at higher pressure**, 478, 484  
     **disintegration**, 396  
     **fluorescence spectrum**, 234  
     **intermediary product of hydrocarbon combustion**, 378, 466, 491–493  
     **reaction product in hydrocarbon combustion**, 368  
**Formaldehyde oxidation, chain reaction**, 378  
     **photochemical reaction**, 379, 380  
     **reaction mechanism**, 379  
     **reaction products**, 379  
**Formic acid**, 406, 407  
**Free length of path**, 249  
**Freedom, degrees of**, 256  
**Frequency, influence of, on the ignitibility of electrical discharges**, 354  
     **of the oscillations in combustion in tubes**, 103–106

## G

- Gas flow in the Bunsen flame, 74, 79-83
  - in detonation, 172
  - in diffusion flames, 211, 213
  - in the engine, 240, 506, 526
  - in industrial firing, 215-218
  - in the progression of explosions, 66, 93, 101, 136, 142, 144, 145
- Gas oil, 577, 582
- Gas phase deactivation, 269*ff.*, 291, 300
- Gas temperatures, measuring technique, 219
- Gas vibrations, in combustion processes, 92, 103-106, 142, 143, 159, 161, 162, 569
  - in knocking combustion, 521-523
- Gasoline, ignition temperature, 45
- Glow discharge, 349
- Glyoxal, 390-393, 401, 403, 406
  - absorption spectrum, 399
  - oxidation product of acetylene, 390, 391
- Glyoxal acid, 390
- Glyoxal oxidation, induction period, 390, 391
  - reaction products, 390
  - surface influence, 391
- Gouy's method for determining normal combustion velocity, 70*ff.*, 84-90
- Gravity, influence of on flame velocity, 94

## H

- Half-life period (radioactive period), 244
- HCO-radical in hydrocarbon combustion, 367, 373, 374, 490, 491
  - spectrum, 233, 234
- Heat conduction in auto-ignition, 5*ff.*
  - in the Bunsen flame, 77, 78
  - in the engine, 240, 526, 532-534
  - in explosions in tubes, 95
  - kinetic theory, 249
  - in percussion waves, 164
  - in spark ignition, 47*ff.*, 364
- Heat conduction error in measuring flame temperature, 219
- Heat production, 258
- Heat theory, of flame propagation, 106-113
  - of incipient explosions, 2-32
  - of spark ignition, 46-54
- Heating velocity, 10
- Helium, influence of, on oxygen-hydrogen combustion, 298, 299
- Heptaldehyde, 455, 456
- Heptane (and isomeres), 444, 526, 538, 555, 559, 564, 581
  - auto-ignition by adiabatic compression, 472-475
    - at higher pressures, 475, 478, 485
  - Heptane oxidation, course of the reaction, 244, 457-459, 461-462
    - luminescence and cold flames, 439, 461, 462
- n-Heptane, disintegration constant, 396, 397
- Heptene, 465
- Heptine, 465, 556
- Heptyl alcohol, 441, 456
- Heptylene, 507
- Hexadiene, 555
- Hexane (and isomeres), 460, 462, 465, 475, 478, 487, 547, 555, 559
  - auto-ignition at higher pressures, 475, 478, 487
    - disintegration constant, 396, 397
    - ignition limits in air, 132
    - maximum combustion velocity in mixture with air, 122
- Hexane oxidation, luminescence and cold flames, 439
- Hexene (and isomeres), 465, 555
- HO<sub>2</sub>-radical in oxygen-hydrogen combustion, 326, 328, 490, 491
  - reactions, 317, 318
- Hugoniot-equation, 166
  - curve, 80, 167
- Hydrocarbons, absorption spectra, 399-400
  - auto-ignition at higher pressures, 471-485
    - catalytic oxidation, 367
    - combustibility relative to H<sub>2</sub> and CO, 370
    - disintegration, 394-398
- H-atom exchange, 372
- hydration and dehydration by H- and D-atoms, 373
- ignition by adiabatic compression, 471-485
  - induction periods for ignition by adiabatic compression, 471-473

- Hydrocarbons, influence of, on the flame velocity in oxygen-hydrogen and carbon monoxide, 374, 375  
luminescence in attack by O-atoms, 488  
oxidation stability and size of molecule, 368  
reaction with atomic hydrogen and oxygen, 371-373, 485, 489  
slow oxidation, 367, 374-468
- Hydrocarbon combustion, 367-499  
aid of radicals, 367, 371ff., 485ff.  
autocatalytic reaction, 367, 376  
chain reaction, 368, 490ff.  
course of conversion and reaction velocity, 376  
explosion limits, 368, 388  
induction period, 367, 376, 377  
influence of additions on the induction period, 367  
intermediary products, 373, 377, 378, 490  
luminescence and cold flames, 368, 378, 437-470  
negative temperature coefficient of the reaction velocity, 368  
normal combustion velocities, 375  
Norrish pattern, 404, 405, 485  
reaction products, 367, 370  
spectroscopic observations, 229ff., 371-375  
theory, 485-496
- Hydrocarbon molecule, point of primary attack, 497, 498
- Hydrogen, adsorption and absorption, 311-313  
carbon monoxide-oxygen-(air-) mixtures, detonation limits, 182, 184  
chlorine mixture, pressure rise in bomb explosions, 188  
detonation velocity in mixture with O<sub>2</sub> and N<sub>2</sub>, 174  
favored combustion, 370  
ignition limits in air and oxygen, 111, 129-132  
ignition range of the system NH<sub>3</sub>-H<sub>2</sub>-O<sub>2</sub>, 134, 135  
H<sub>2</sub>-NO-Cl<sub>2</sub>, 134  
influence on ignition temperatures, 42ff.  
maximum combustion velocity in mixture with air, 123
- Hydrogen, oxygen mixtures, detonation pressure, 189  
flame path up to inception of detonation, 186  
influence of temperature on detonation, 186  
pre-detonation path, 190  
oxygen-(air-)mixtures, detonation limits, 184  
pressure rise in explosion in mixture with air and CO, 156  
(See also Oxygen-hydrogen)
- Hydrogen atom, presence in oxygen-hydrogen combustion, 321-330  
reaction with hydrocarbons, 371ff.  
reactions, 316-318  
role, in hydrocarbon combustion, 367, 371ff.  
in reactions in discharges, 352
- Hydrogen flame, spectrum, 229
- Hydrogen phosphide oxidation, 290, 291  
explosion limits, 290
- Hydrogen sulphide-air mixture, explosion limits, 290  
ignition limits, 132  
ignition temperature, 45  
reaction with oxygen, 20
- Hydrogen superoxide, 407, 409, 417, 434, 435, 496  
production in atomic reactions, 318, 319  
in oxygen-hydrogen combustion in discharges, 349  
reaction product in hydrocarbon combustion, 367
- Hydrogen-air mixtures, flame temperature, 223  
ignition by heated pellets, 30  
ignition temperatures, 35ff.
- Hydroxylations in hydrocarbon combustion, 370, 393
- Hydroxy-methyl-acetyl peroxide, 545
- Hydroxytoluol, 470

I

- IG testing engine, 536
- Ignitibility by various forms of discharge, 348, 354ff.
- Ignition, by adiabatic compression, 19, 33ff., 471ff.  
definition of, 4

- Ignition, forced, 19**  
by heated surfaces, 22-33  
penetration through narrow slit, 101  
by sparks, 47-59, 346-366
- Ignition delay, 36f.**  
in the Diesel engine, 571, 577ff.  
influence of temperature, 577, 585, 586  
in spark ignition, 156  
(See also Induction period)
- Ignition energy, 128**
- Ignition limits, 13, 64, 84, 124-135**  
dependence of, on pressure, 129-131  
on spark energy, 359  
on temperature, 129  
on type of ignition, 128  
determination of, 128, 129  
of fuel-air and fuel-oxygen mixtures, 110  
influence of additions, 133-135  
of mixtures, 131, 132  
in spark ignition, 128
- Ignition point, 548-550**  
(See also Ignition temperature)
- Ignition point tester, 485, 569, 580**
- Ignition process in the Diesel engine, reaction kinetics, 583-587**
- Ignition ranges, narrowing and widening of by pressure, 129-131**  
ternary, 134, 135
- Ignition temperature, definition of, 3, 7, 113**  
experimental material, 32-45, 292ff., 331, 367
- Ignition velocity, 64**
- Illuminating gas, air mixture, ignition by heated pellets, 29**  
flame temperature, 223
- Impact number, 247ff.**  
and reaction velocity, 254, 255
- Indene, 558**
- Indicator, for measuring knocking behavior, 536, 537**
- Indicators, for pressure measurement, 530, 531**
- Inductance component in spark ignition, 346-348, 355-357**
- Induction period, in chain explosion, 281**  
in hydrocarbon combustion, 367  
influence of additions, 367
- Induction period, in oxygen-hydrogen combustion, 292, 293, 306, 307**  
and reaction pattern, 324  
in thermal explosion, 10, 18  
(See also specific substances)
- Industrial firing (see Flames of non-premixed gases)**
- Inert gas additions in diffusion flames, 213, 214**  
(See also specific substances)
- Inert gases, influences of, on the combustion velocity, 111-113**
- Initial ignition, producing a quasi-detonation, 188**
- Injection process in the Diesel engine, 574-576**
- Inner cone of the Bunsen flame, 70ff., 236**
- Instability surface in percussion waves, 164**
- Interior friction of gases in percussion waves, 164**  
kinetic theory, 249
- Intermediary gas in the Bunsen burner, 83, 236, 237**
- Iodine, 413, 417, 422, 543, 549**  
influence of, on carbon monoxide combustion, 335  
on oxygen-hydrogen combustion, 303, 329, 330
- Ion movement, influence of, on flame velocity, 366**
- Ion reactions, 456**
- Ionization, of the flame gases, 62**  
in flames, 366
- Ionization potential, influence of, on the reactions in discharges, 362, 363**
- Ionization process, for measuring the flame velocity in the engine, 506**
- Iron carbonyl, anti-knock, 502, 539, 548, 567**
- Isoamyl bromide, ignition range of the system CH<sub>4</sub>-air-iso-amylobromide, 135**
- Iso-octane (see Octane)**
- K**
- Ketones, 498**  
absorption spectrum, 399
- Kinetic gas theory, 247-258**

**Kinetics, of combustion and explosion**  
     processes, 242-291  
     fundamentals, 242-247  
**Kirchhoff's law**, 235  
**Knocking**, 186, 430, 437, 462, 473, 501-503, 508-535  
     chain reaction, 544  
     and detonation, 518-523  
     explanation, 518-523, 569-570  
     inception, dependence of, on ignition moment, 532, 533  
     computing of, from auto-ignition behavior, 510  
     index of fuels, 581  
     influence, of the form of the cylinder head, 520  
     of overloading, 533, 534  
     investigation of pre-reactions, 538-547  
     origin of in the engine, 501-503  
     separation of fuel and engine factors, 570  
     spectroscopic phenomena, 239  
**Knocking behavior**, measurement, 535  
**Knocking combustion**, in experimental apparatus, 511, 513  
     flame intensity, 519  
     flame pictures of the engine, 513-514, 516, 517, 521-522  
     gas vibrations, 530-532  
     indicator diagrams, 512, 532  
     influence of, on performance and efficiency of an engine, 528-532, 540  
     and percussion waves, 532  
     peak pressures in the engine, 527*ff.*  
     percussion waves, 512, 519-523, 527*ff.*  
     thermal demands on the engine, 532  
     velocity, 512, 519, 527  
**Knock-promoters**, 502, 544, 550, 562  
     chemical structure, 550  
**Knock-resistance**, and branching, 559  
     of a fuel, 536  
     influence of double bonds, 547, 548  
     and luminescence, 440  
     and mixtures, 562-564

## L

**Laminar flow** in the Bunsen burner, 75-77, 82  
**Latent energy** in explosions, 225

**Lead**, 547  
**Lead tetraethyl**, anti-knock, 502, 512, 538, 540, 542, 545, 547, 549, 557, 560-562, 565-569  
     change of the predetonation path, 190, 191  
     influence of, on oxidation of hydrocarbons, 45, 367, 387, 443, 444, 465, 477, 499  
**Life period** of free atoms, radicals and stimulated molecules, 315*ff.*, 353  
**Light yields** in chemiluminescence, 239  
**Limit diameter** for flame propagation in tubes, 99-100  
**Line reversal method** for measuring flame temperature, 221-224  
**Luminescence and cold flames**, 234  
     in hydrocarbon combustion, 368*ff.*  
     and knock-resistance, 440  
     temperature dependence, 438, 439  
     (See also specific substances)

## M

**Mass (action) effect** of reaction kinetics, law of, 243  
**Mass conversion velocity**, 146  
**Maxwell's law** of velocity distribution, 251  
**Méker burner**, temperature measurement, 223  
**Mercury**, 305  
**Mesitylene**, 558  
**Metal atoms**, influence of, on the reactions of explosive mixtures, 351, 352  
**Metal compounds**, as anti-knocks, 351, 352  
     (See also Anti-knocks)  
**Metal mist**, 548, 549  
**Metastable condition** of an explosive gas mixture, 301  
**Methane**, air mixture, flame temperature, 223  
     flame velocity in tubes, 99-101  
     ignition by heated surfaces, 25, 29  
     by sparks, 55-59  
     auto-ignition at higher pressures, 479, 487  
     combustion velocity in various atmospheres, 112, 113

- Methane**, critical compression ratio, 555  
disintegration constant, 396  
ignition limits in air and oxygen, 110, 129, 130, 131  
ignition range of the system  $\text{CH}_4$ -air-isoamylbromide, 135  
maximum combustion velocity in mixture with air, 122  
octane number, 559  
reaction with atomic hydrogen and oxygen, 372, 373  
**Methane flame**, spectrum, 235  
**Methane oxidation**, activation energy, 422  
explosion limits, 416, 479  
induction period, 412, 413, 417*ff.*  
influence of additions, 412, 417-419  
of container dimensions, 417  
intermediary products, 411  
luminescence and cold flames, 437, 439  
methanol formation, 378, 415, 416  
reaction mechanism, 416, 485-489  
reaction products, 371, 414*ff.*  
**Methanol**, 429, 433, 435, 507, 560  
auto-ignition at higher pressures, 484  
disintegration, 396  
formation in ethane and methane oxidation, 378, 415, 416  
**Methanol flame**, spectrum, 235  
**Methanol oxidation**, luminescence, 440  
**Methyl amyl ether**, 559  
**Methyl amyl cyclohexane**, 557  
**Methyl butene**, 555  
**Methyl butyl cyclohexane**, 557  
**Methyl butyl ether**, 559  
**Methyl cyclohexane**, 465, 557, 558  
**Methyl chloride**, 489  
**Methyl ethyl cyclohexane**, 557  
**Methyl ethyl cyclopentane**, 557  
**Methyl ethyl pentane**, 457  
**3-Methyl heptane**, 457  
**Methyl hexene**, 555  
**Methyl iodide**, 489  
absorption spectrum, 399  
**Methyl naphthalene**, 580, 587  
**Methyl nitrite**, 21, 418, 426  
**Methyl phenyl acetylene**, 558  
**Methyl propyl cyclohexane**, 557  
**Methylene chloride**, 489  
**Methyl-iso-propyl cyclohexane**, 557  
**Methyl-iso-propyl ether**, 559  
**Mixed octane numbers**, 564, 565  
**Mixing process**, in the Diesel engine, 574, 575  
in flames of non-premixed gases, 210  
Mixture limit for the appearance of explosion, 13  
Mixture ratios, in the burner when using the batswing burner, 215-218  
Model experiments for the mixing process in commercial firing, 216  
Molecular diameter, 249  
Molecular velocity, 249  
Molecularity of a reaction, 244  
Monochloro-naphthalene, 443  
Monoethyl hydrogen superperoxide, 545  
Monohydroxy-alkyl peroxide, 545
- N
- Naphthalene**, absorption spectrum, 399  
**Naphthene**, 558, 562  
cold flames in oxidation, 234  
**Naphthene oxidation**, luminescence and cold flames, 437*ff.*  
**Natural gas-air mixtures**, ignition by heated surfaces, 26, 27  
**Negative catalysis**, 380  
**Nickel carbonyl**, 567  
**Nitric oxide**, 135, 160, 235, 239, 334, 336, 406, 463  
**Nitrites**, 502, 544, 569, 583  
**Nitrogen**, 37*ff.*, 334, 337*ff.*, 430-432, 450, 453, 454  
**Nitrogen dioxide**, 303, 330, 399, 404, 418, 422, 451, 543  
**Nonane**, 462, 465  
**Normal combustion velocity**, 62*ff.*  
absolute computation, 120, 121  
application of the theory to oxygen-hydrogen reaction, 324  
from bomb explosions, 148  
influence, of addition of anti-knocks, 122, 123  
of diffusion and heat conduction, 116-117  
of fuel concentration, 123, 124  
of inert gas, 111-113  
of iron carbonyl additions, 122, 123  
of temperature and pressure, 89-91  
of carbon monoxide-air mixtures with varying  $\text{H}_2\text{O}$  content, 121



Normal combustion velocity, comparison of the influence of diffusion and heat conduction, 116-117  
 of theory and experiment, 120  
 of  $H_2-O_2-N_2$  mixtures, 123, 124  
 in hydrocarbon combustion, 375, 376  
 measuring methods, 67-74, 84  
 of methane-air mixtures in tubes, 99  
 numerical values, 63, 72, 73, 123, 124  
 of ozone-oxygen mixtures, 120  
 and reaction velocity, 121-124  
 strict theory, 117-119  
 theory of heat, 106-110

## O

- Octane (and isomeres), 526, 555, 559, 567  
 auto-ignition at higher pressures, 475, 478, 479, 486  
 ignition by adiabatic compression, 475  
 induced oxidation, 459, 460  
*i*-Octane, disintegration constant, 397  
*n*-Octane, disintegration constant, 396, 397  
 Octane number, 527, 559, 580  
 Octane oxidation, course of reaction, 457, 462, 465-467  
 luminescence and cold flames, 440, 442, 455, 457  
 reaction products, 454, 465, 466  
 Octene, 555  
 influence of, on aldehyde oxidation, 387, 467  
 Octine, 556  
 OH-bands, appearance of, in carbon monoxide combustion, 334, 339  
 OH-radical, appearance of, in oxygen-hydrogen combustion, 315, 321*ff.*, 351-353  
 band spectrum, 229  
 intensity distribution of the bands, 230  
 optical concentration, determination of in flames, 231, 321, 322, 325  
 reactions, 320, 321  
 role, in CO-combustion, 344, 351  
 in hydrocarbon combustion, 367, 491  
 self-reversal of the bands, 229  
 spectroscopic investigation, 321*ff.*  
 Olefins, 433, 467, 560  
 critical compression ratio, 555  
 disintegration, 396  
 Olefins, influence on phosphorus oxidation, 289  
 luminescence and cold flames in oxidation, 234, 437, 439  
 oxidation stability, 456  
 Optical temperature measurement, of flames, 220-223  
 in the engine, 239  
 Order of a reaction, 244  
 Oscillator, harmonic, 253  
 Otto engine, combustion, 501-571  
 compression ratio and combustion velocity, 509  
 and efficiency, 501-506  
 flame velocity, 506, 542  
 gas-analytical investigation of combustion, 539-542  
 influence of dissociation on efficiency, 507  
 knocking, 501-503, 509-570  
 optical temperature measurement, 223  
 overloading, 501  
 phenomena of combustion and knocking processes, 525-535  
 slow motion pictures of combustion, 515-517  
 spectroscopic investigation of combustion, 539, 551-553  
 temperature distribution after combustion, 527  
 thermal efficiency and mixture composition, 508  
 thermodynamics of combustion, 503-508  
 Outer cone of the Bunsen flame, thermal radiation, 237  
 Overloading, influence of, on appearance of knocking, 533, 534  
 in the Otto engine, 501  
 Oxidation (*see* specific substances)  
 Oxygen, adsorption, 313  
 influence of, on slow carbon monoxide combustion, 335, 336  
 Oxygen atom, reactions, 319-320  
 with hydrocarbons, 374, 484, 488  
 role, in hydrocarbon combustion, 372*ff.*  
 in oxygen-hydrogen combustion, 323  
 in reactions in discharges, 352  
 Oxygen flame in hydrogen atmosphere, spectrum, 229

- Oxygen-hydrogen, detonation with additions of He and A, 176  
detonation velocity, 179  
ignition by platinum, 26  
Oxygen-hydrogen combustion, atom and radical concentrations, 321-325  
autocatalytic reaction, 308  
catalytic reaction, 292, 308  
chain breaking reactions, 293*ff.*, 326-330  
chemiluminescence, 324  
deactivation of chain agents (*see* Chain breaking)  
in electrical discharges, 349*ff.*  
energy of emitted radiation, 324, 325  
explosion limits, 292-305  
ignition by heated pellets, 30  
ignition limits for sparks of varying energy, 359  
ignition temperatures, 35*ff.*, 303*ff.*  
induction periods, 292, 304, 305  
influence, of adsorption processes, 312-316  
of the composition on the explosion limits, 298, 300  
of the container dimensions on the lower explosion limit, 293-297  
of deuterium, 301  
of foreign gas additions, 294-299, 300, 302, 308, 309, 329, 330  
of the wall material, 294, 310, 331  
kinetics, 323  
photographic recording, 306  
in the presence of atomic hydrogen and oxygen, 303-305  
reaction mechanism, 264, 292-330  
reaction outside the explosion limits, 306-314, 330, 331  
reaction scheme, 323, 324  
reaction velocity, 306-315, 323, 324  
spectrum, 324, 326  
temperature dependence of the explosion limits, 297*ff.*, 329  
theory of the explosion limits, 326-330  
third explosion limit, 306  
time factor in development, 305, 306  
wall influence, 291, 294-299, 300, 309-314  
Oxygen-hydrogen explosions, photochemical induction, 305  
Ozone, 409, 416, 502, 544, 569  
aid in atomic reactions, 319, 320  
formation in phosphorus oxidation, 288  
participation in carbon monoxide combustion, 343  
Ozone formation in flames, 319  
Ozone-oxygen mixture, combustion velocity, 120, 148
- P
- Parachor of fuels, 581, 582  
Paraffins, critical compression ratio, 555  
disintegration constants, 396  
ignition limits in air, 132, 471*ff.*  
ignition temperatures, 45, 46, 410*ff.*, 471*ff.*  
influence of anti-knocks on combustion, 555, 560, 561  
octane numbers, 559  
oxidation stability, 456, 458  
reactions with atomic hydrogen and oxygen, 372-373  
(*See also* individual substances)  
Paraffin oxidation, in the liquid phase, 456  
luminescence and cold flames, 234, 437*ff.*  
Parahydrogen, 321  
Pentane (and isomeres), 461, 462, 464, 555, 559  
absorption spectrum, 399  
air mixtures, ignition by heated pellets, 30  
ignition by adiabatic compression, 475, 478, 487  
maximum combustion velocity in mixture with air, 121  
reaction with atomic hydrogen and oxygen, 373, 374  
Pentane oxidation, activation energy, 448, 450  
induction period, 448, 449  
influence of additions, 450, 451, 460  
luminescence and cold flames, 438, 439, 444-457  
reaction mechanism, 448  
temperature coefficient, 449  
Pentane-oxygen-(nitrogen-) mixtures, auto-ignition at higher pressures, 474, 475, 478, 487

- Pentane-oxygen-(nitrogen-)mixtures,**  
     detonation velocity, 179  
     disintegration constant, 396  
     ignition limits in air, 130  
     predetonation path, 190, 191, 192  
**Pentene,** 460, 555  
**Peracids,** 422, 496  
**Peracetic acid,** 387  
**Perbenzoic acid,** 381  
**Percussion wave,** 140-142, 163-173  
     change of condition in, 166  
     effect on a flame, 196, 197  
     and flame front, 198  
     in knocking combustion, 512, 518-523, 527*ff.*  
**Perhydrol,** 537  
**Peroxide radicals,** 393, 493  
**Peroxides,** 422, 429, 434, 461-464, 493-496, 502, 569, 583  
     influence on knocking, 545-547  
     intermediary products in engine combustion, 541-544  
     reaction products in hydrocarbon combustion, 368  
**Perpropionic acid,** 390  
**Phenol,** 460, 469  
     absorption spectrum, 399  
**Phenyl acetylene,** 558  
**Phenyl butadien,** 558  
**Phenyl ethylene,** 558  
**Phenyl-methyl-carbinol,** 470  
**Phosphorus oxidation,** 284-290  
     explosion limits, 284-290  
     influence, of additions, 284, 288, 289  
     of container dimensions, 285  
     of pressure, 285  
     outside the explosion limits, 289  
     surface reactions, 289  
     theory of the explosion limits, 284-288  
**Photochemical induction of explosions,** 305  
     reactions, 262, 315-320  
**Planck's law of radiation,** 235  
**Platinum,** catalytic effect, 25, 26  
**Polymerization process in soot formation in flames,** 232  
**Potassium,** 548, 549  
**Potassium chloride,** influence of wall covered with on oxygen-hydrogen combustion, 295, 311-314, 330  
**Predetonation path,** 190-192  
**Pressure indicators,** 145  
**Pressure jump in the burning surface,** 80  
**Pressure limit for spontaneous explosions,** definition of, 13  
**Pressure recording in explosions in closed containers,** 142, 145*ff.*  
**Pressure rise and flame velocity,** 145*ff.*  
**Propane,** 464, 555, 559  
     auto-ignition at higher pressures, 479, 486, 487  
     disintegration constant, 396  
     explosion limits, 479, 486  
     oxygen mixtures, detonation limits, 183, 184  
     detonation velocity, 179  
     reaction with atomic hydrogen, 373  
**Propane oxidation,** activation energy, 436  
     cold flames, 428, 438  
     induction period, 429, 430  
     influence of additions, 428-430, 435  
     reaction mechanism, 428, 429  
     reaction products, 428, 429, 433-435  
     surface influence, 427-433  
     temperature coefficient, 428, 435  
**Propanol, auto-ignition at higher pressure,** 486  
**Propanol oxidation, luminescence,** 441  
**Propionaldehyde, auto-ignition at higher pressures,** 486  
**Propionaldehyde oxidation, reaction products,** 390  
     reaction velocity, 389  
     wall influence, 390  
**Propyl benzol,** 558  
**Propyl-butyl ether,** 559  
**Propylene,** 435, 555  
     auto-ignition at higher pressures, 487, 488  
     ignition limits in air and oxygen, 110, 132  
     maximum combustion velocity in mixture with air, 122  
**Propylene oxidation,** 407  
**Pseudodetonation,** 517

## Q

- Quarter-life span,** 244  
**Quasi-detonation,** 188  
**Quasi-molecule, life span,** 262

**Quasi-stationarity of the concentration of active particles, 260**

**Rotation vibration spectrum of the water molecule, 229**

**R**

**Radiation, elimination of, by additions of foreign gases and pressure, 238**  
**in the engine, 239, 539, 551-553**  
**investigation of, in flames, 227-241**  
**source of error in measuring flame temperatures, 219**  
**Radiation losses in bomb explosions, 238**  
**Radiation processes (see Gas flow)**  
**Radiation properties of combustion gases, 239**  
**Radicals, emission spectrum, 229**  
**free, reactions, 314-321**  
**role in chemical reactions, 229, 259**  
**in hydrocarbon combustion, 367, 370ff.**  
**in oxygen-hydrogen combustion, 321-326**  
*(See also specific substances, Reaction mechanism)*  
**Reaction, almost isothermic, 17**  
**Reaction equation and chain pattern, 259, 260**  
**Reaction kinetics (see Kinetics)**  
**Reaction mechanism, complex, 247**  
**Reaction pattern and induction time, 323**  
**Reaction types, 244**  
**Reaction velocity, in the burning zone, 114ff.**  
**in chain branching, 267ff.**  
**and equilibrium constant, 257, 258**  
**in exothermic reaction or explosion, 15**  
**and impact number, 255, 257**  
**importance for detonation, 172, 173, 174, 179-181, 206-209**  
**and normal combustion velocity, 121-124**  
**and spin of detonations, 201**  
**temperature coefficient, 245, 246**  
**Recombination of atoms and radicals, 259, 261, 262**  
**Refraction index of fuels, 581**  
**Resistance thermometer for measuring flame temperature, 219-221**  
**Reynolds number, 80ff.**

**S**

**Safety lamp, 103**  
**Schlieren photograph, 140, 141, 177, 198**  
**of the Bunsen burner, 81**  
**Selenium, 548, 549**  
**Selenium diethyl, 387**  
**Sensitized light reactions, 304, 315**  
**Serruy's indicator, 530, 531**  
**Siemens-Martin furnace, gas-mixture ratios, 215**  
**Similarity, law of, in model experiments on industrial firing, 217**  
**Slow-motion, for flame photography, 92**  
**Slow-motion photography of engine combustion, 516-517**  
**S<sub>x</sub>-molecule, spectrum, 235**  
**SO-molecule, spectrum, 235**  
**Soap-bubble method for measuring normal combustion velocity, 67-70**  
**Sodium, 548**  
**Soot-formation, in hydrocarbon combustion, 369**  
**influence of, on flame spectrum, 232**  
**mechanism, 232**  
**Spark, diameter of, 54**  
**energy, 55**  
**influence of, on ignition limits, 128**  
**Spark discharge, oscillograph, 346, 354, 355**  
**Spark ignition, 47-61, 346-366**  
**capacity component, 347, 354-356**  
**diffusion processes, 49, 363**  
**in the engine, 360-361**  
**heating equation, 50**  
**inductance component, 347-349, 354-356**  
**inductor and condenser discharge, 60, 347-349**  
**minimum current intensity, 56-59, 346ff.**  
**spread of combustion, 48ff.**  
**temperature distribution, 51ff.**  
**theory of heat, 47-61**  
**theory of non-thermal combustion, 362-366**  
**Specific heats of gases, 227**

- Spectroscopic investigations, on the  
   Diesel engine, 589  
   on flames, 229-235  
   on the Otto engine, 539, 551-553  
 Spectrum of hydrocarbon flames, 231*ff.*,  
   371-375  
 Spin, pitch of, in detonations, 193  
 Spin phenomenon, detonations, 192-201  
 Static explosions, 65, 70  
 Steric factor, 257  
 Stimulated molecules as chain agents,  
   267-269  
 Substance chains, 268  
 Sulphur, 548  
 Sulphur combustion, 290  
 Sulphur compounds, 543  
 Swan spectrum, 232-234

## T

- Technical or industrial firing (*see* Flames  
   of non-premixed gases)  
 Tellurium, 548, 549  
 Temperature, in the engine, 223, 239-  
   241, 525  
 Temperature coefficient of the reaction  
   velocity, 245, 246, 264, 367  
 Temperature radiation, in the engine,  
   223, 240, 525  
 Test engines, 536  
 Tetradecane, 465  
 Tetraline peroxide, 583  
 Tetratriacontadiene, 581  
 Thallium, 548, 549  
 Thermal capacity and combustion ve-  
   locity, 111  
   of the walls of the tube, influence on  
   flames, 100-102  
 Thermal conductivity and combustion  
   velocity, 111  
   of the walls of the tube, influence on  
   flames, 100-102  
 Thermal explosion, 3*ff.*  
   development in time, 10  
   examples of, 20, 419  
   heterogeneous mixtures, 14  
   induction period, 10  
   rise in temperature, 10, 20  
   special cases, 14  
 Thermal radiation, 20  
   of flames, 235-239

- Thermo-element for temperature meas-  
   urement of flames, 219-220  
 Tin tetraethyl, 567  
 Titanium tetrachloride, 567  
 Toluol, 462, 469-472, 558  
 Toluol oxidation, luminescence, 439  
 Trimethyl butane, 555  
 Triethyl butene, 555  
 Trimethyl pentane, 457, 555  
 Trimethyl pentene, 555  
 Trimethyl phenylallene, 558  
 Triple collision, 262  
 Turbulence, in the Bunsen flame, 80-81  
   in the engine, 240, 506, 526  
   in flames of non-premixed gases, 210,  
   213-218

## U

- Ultra-red radiation, means of determin-  
   ing temperature, 222  
 Unburned mixture, reaction and auto-  
   ignition in engine, 517, 523, 539  
   temperature in the engine, 526  
 Undecane, 462  
 Unsaturated hydrocarbons, 45, 46, 132,  
   234, 290, 293, 433, 437, 439, 456,  
   467, 555, 560  
   (*See also* specific substances)

## V

- Vaidya bands, 230-234  
 Velocity coefficient of chemical reactions,  
   242-246  
   physical significance, 246*ff.*  
 Velocity jump in the burning surface, 80  
 Velocity laws of various types of reac-  
   tion, 243-247  
 Vibration quantum, 252

## W

- Wall, influence of reactions, 246, 262*ff.*  
   (*See also* specific substances)  
 Wall material, influence of, on flame  
   propagation, 100-102  
   in reactions (*see* specific substances)  
 Water gas equilibrium, in the Bunsen  
   flame, 237  
   in hydrocarbon combustion, 369

- |  |   |
|--|---|
| <p><b>Water vapor, adsorption, 312, 313</b><br/>             influence of, on carbon monoxide combustion, 331, 332, 339, 342<br/>             on detonation velocity of <math>2\text{CO} + \text{O}_2</math>, 180<br/>             on the explosion limits in carbon monoxide combustion, 332<br/>             on the flame velocity of carbon monoxide-air mixtures, 121<br/>             on oxygen-hydrogen combustion, 302, 303, 307, 308<br/>             on radiation in carbon monoxide combustion, 332, 336</p> | <p><b>Water vapor bands, 229, 231, 326</b><br/> <b>Welding burner, temperature measurement, 223</b><br/> <b>Wire probe for measuring flame temperature, 222</b></p> |
|--|---|
- X
- Z
- Zinc, 548